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RESEARCH ON COLORANT SYSTEMS WHOSE
CHARACTERISTICS MAY BE REVERSED

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TECHNICAL REPORT

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**RESEARCH ON COLORANT
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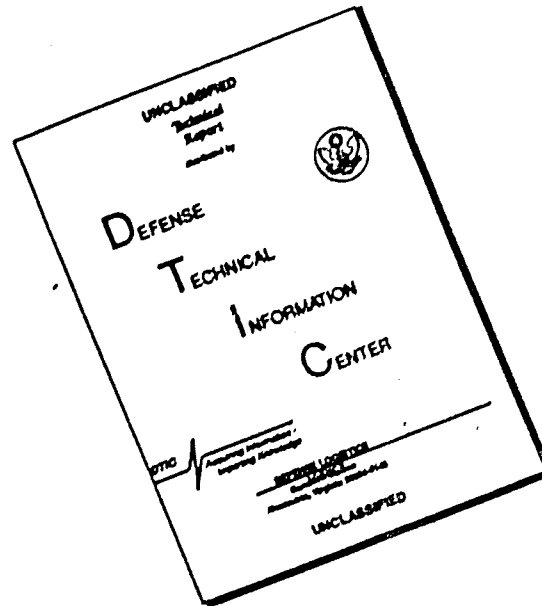
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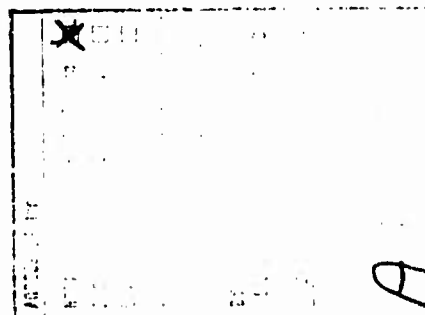


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SUMMARY

Objective

1. To perform chemical and physical research on colorant systems whose reflection and absorption spectra are capable of being altered in a continuously variable, reversible, and controllable manner by the application of modest electrical potentials or powers.
2. Emphasis shall be given to compounds that can be used in systems that are potentially capable of being modified for use in a flexible lightweight form such as a textile fabric. The long range purpose of the research is to find suitable materials and means for using them in systems of clothing having passive counter-surveillance properties in the visible region of the electromagnetic spectrum.
3. The research shall consider all possible approaches to an electrically activated colorant system, except those noted in paragraph 5. The Contractor shall determine the chemical and physical characteristics of the approach investigated, including spectral absorption or reflection changes upon application of electrical stimuli, forward and return rates of spectral changes, voltage and power requirements and evidence of deterioration on repeated cycling.
4. The scope of research shall include but not be limited to studies of electrochemical reactions (e.g. redox reactions) that produce suitable color changes. Such electrochemical reactions, however, must not produce gases, unless means for eliminating problems caused by their production in ultimate use are clearly available. The research shall also include an investigation of solid substances that may respond favourably to electrical stimuli by means other than electrochemical reactions.
5. The research shall not include the following approaches:
 - (a) Approaches that depend on temperature changes for changes in spectral properties (thermochromism)
 - (b) Approaches that depend directly on exposure to light for spectral properties (photochromism)
 - (c) Approaches based on a need for high current densities or on high levels of electrical potential (electrochromism, Stark effects)
 - (d) Approaches based on dynamic scattering of nematic crystals
 - (e) Approaches that have a high probability that proposed systems will pose problems involving weight, discomfort, high power requirements, or hazards to a potential user.



DIGEST OF THE REPORT

The work in this report was guided by the principle that any color can be produced to an observer at a distance by the correct pattern of colored areas of three primary colors, which for additive color processes are green, cyan (blue), and magenta (red), or for subtractive color processes, the well-known primaries of red, yellow and blue. If the display of three colors can be masked or displayed by electrical methods, the observed pattern of color necessary for the required camouflage can be changed at will. The actual pattern will depend on the pattern of electrical connections to the numerous cells making up the display.

The objective of the work based on this principle was to try to find shutter systems to mask or display color by electrical methods, or to produce the required color changes directly by electrical means. The systems investigated were as follows:

- (i) Shutter systems based on the Kerr electro-optical effect.
- (ii) Shutter systems based on the movement of magnetic particles by electro magnetic methods.
- (iii) Shutters based on electroplating effects that can be reversed.
- (iv) Color changes, or shutter effects by the electro-chemical operation of redox systems with or without additional indicator colors.

The achievement of the main objectives of the contract can therefore be conveniently summarized under these four sections.

Kerr Electro-Optical Effects

The principle of the Kerr effect is that suitable liquids placed in an electrical field behave optically like a uniaxial crystal with the optic axis parallel to the field direction. Plane polarized light passed through such a system becomes elliptically or circularly polarized and therefore is not blocked by a second polariser crossed with the first. Thus, whilst the electrical field is operative, light passes through the system, and does not (due to the crossed polars) when the field is turned off. For camouflage, the best system is one operating on reflected light, and this can easily be arranged by a combination of a colored polarizing screen and a quarter wave plate placed in front of a Kerr cell backed by a highly reflecting surface.

Up to date, the best liquid to place in the Kerr cell is the well-known liquid, nitrobenzene, and a demonstration was made to show that the expected phenomena were observed. The magnitude of the Kerr effect is determined by the Kerr constant, j , of the liquid in the cell, which is given by the equation:

$$\Delta = j \frac{lE^2}{d}$$

where Δ is the path difference in wavelengths λ , l the electrode length in metres, d the electrode separation in metres and E the applied voltage in volts. Since j for nitrobenzene is $2.44 \times 10^{-12} \text{ mV}^{-2}$ this equation was used to find the critical dimensions and voltages for use with such shutters. For instance, a cell 4 cm long with an electrode separation of 0.1 mm requires an operating voltage of 160v. Such a cell could not be used for textile application, so calculations were made to find the feasibility of cells for clothing camouflage. Graphs were produced relating the cell length, field strength, breakdown strength of nitrobenzene, and the supply voltage. It was found that for cells less than 1 mm long the field strength exceeded the breakdown strength of the nitrobenzene. The conclusion was reached that for clothing the necessary voltages for small cells were too high, and large cells with more workable voltages were impractical. If a liquid (or solid) could be found with a much larger Kerr constant than nitrobenzene, then this conclusion would be incorrect, but until such substance can be found, the Kerr effect can not conveniently be used for clothing camouflage, although its use for larger objects may be feasible.

Electromagnetic Shutters

Experiments were conducted with iron particles and particles of magnetic iron oxide; the latter proved to be the better. The particles were suspended in liquid paraffin in a small tray above an electromagnet. On switching on the current the iron oxide particles oriented along the direction of the magnetic field and a high light transmission difference (L.T.D.) was obtained. Within five seconds of switching off the field, the movement of the particles under gravity produced a low light transmission. A second solenoid aligned at 90° to the first helped to settle the particles horizontally and increased the shutter effect. However, the difficulty of the system is the re-dispersal of the particles if the cell is too deep. Improvement in the system was achieved by the use of small pieces of polystyrene in which magnetic iron oxide was embedded. The chief problem of re-dispersal, however, remained, and, in view of the inconvenience of the cells and the high value of the magnetic field strength required to operate them, it was decided that this approach to the camouflage problem was not a profitable one. In view of the successful operation of other devices described in this report, the pursuance of the electromagnetic system was suspended as being of low priority.

Transparent Electrodes

Consideration of the requirements for camouflage purposes showed that it was advantageous to use transparent electrodes in the development of the electroplating and redox systems. Experiments were therefore carried out on methods to produce such electrodes. One method was to heat a glass substrate to 430°C and then to play on it a stream of sublimed stannous chloride carried in a stream of oxygen to produce a conducting transparent tin oxide layer on the glass. Use was also made of a commercial transparent electrode material known as Baltracon. Since glass electrodes are not suitable ultimately as electrodes in clothing applications, other methods, such as suitable lacquers, were also investigated for use as electrodes. Further investigation into this area of the problem is still required.

Reversible Electroplating Cells

A very promising system for shutter operation was found based on electrolysis without the production of gas. In a cell constructed from transparent electrodes, complete cut-off of light was achieved in less than a second with a cell 1 mm thick and a working voltage around 10v. Reversal took place readily, and multiplicity of reversals was established. The working solution consisted of a mixture of silver iodide, caustic soda and sodium iodide. In operating this cell it is desirable to arrange for a small current to flow continuously to facilitate reversal, and suitable circuits were designed based on the use of a pulse generator. It was found that up to 1.0 volt, Ohms law was obeyed, but above 2 volts the current through the cell was proportional to $V^{1.5}$, which indicated a space-charge limited current. The conditions of deplating and the light transmission characteristics of the cell were also determined. It was predicted from theory that the thickness of silver to operate the cell was 200 Å, and the alternative metals to silver were tin or cadmium. To get uniform plating it was necessary to control the plating rate, and the composition of the electrolyte was critical. Furthermore, to get uniform parallel current flow lines in the electrolyte, the width of the aperture of the cell had to be controlled. A theory was developed that predicted the maximum usable shutter widths possible with transparent electrodes. To realize large area of shutter action as required in camouflage it is necessary to

- (a) use multiple cells
- (b) use transparent electrodes of high conductivity
- (c) use electrolytes with low conductivity.

Experiments were carried out to investigate these conditions, and a successful cell was produced.

On the advice of the Contracting Officer, further work on these cells has been suspended in favour of developing to the full the redox systems described in the main body of the report. This decision is in accordance with the conditions laid down in the contract.

Redox Systems

It is necessary to define oxidation and reduction in terms of electrochemical usage. Oxidation is defined as the loss of electrons, and reduction by the gain of electrons. An oxidizing agent is thus one that accepts electrons and is itself reduced; a reducing agent, one that supplies electrons, itself being oxidized. At an anode of a cell, electrons are discharged, and oxidation thus takes place in the surrounding solution, whereas the reverse; i.e., reduction, takes place in the vicinity of the cathode. If, therefore, redox systems are to be used for producing color changes electrically, it is necessary to find systems to which these electrochemical principles can be applied.

In the early experiments two types of chemical redox systems were investigated, one in which only one redox reaction was concerned, and the other where two redox reactions interacted. Theoretical titration curves were derived by the application of the equation:

$$E = E^0 + \frac{RT}{nF} \cdot \ln \left(\frac{a_{ox}}{a_{red}} \right)$$

where E is the electrochemical potential; E^0 , the potential of the transition point, viz that point at which the activities (a_{ox}) balance those of (a_{red}); R is the gas constant; T, the absolute temperature; n, the number of charges involved; and F, the Faraday constant. Only with a dual system was a sharp transition given, and since it is at this point that suitable redox indicators change color, the use of a dual system appeared to be the more promising for camouflage purposes. Electrochemical titration in suitable cells established the range of voltages required to drive specific reactions electrically. Systems investigated included ferrous/ferric with cerous/ceric, iron gallate, stannous/stannic with iodine in potassium iodide, ferrocyanide/ferricyanide with iodine in potassium iodide and others. Difficulties encountered in driving these systems electrically were traced to type of electrodes, design of cells and other factors. It was found that small cells with carbon electrodes separated by a sintered disc worked successfully in both directions. A cell containing 0.2M potassium ferrocyanide and 0.2M potassium ferricyanide in 0.1 to 1.0 N sulphuric acid with 0.2M iodine in 10% potassium iodide together with a polyvinyl alcohol indicator (Blue - Yellow: for iodine) was successfully operated. The working voltage was 1.4v, and the time of reversal 4 minutes.

Another successful system was 0.04M ferrous ammonium sulphate in 1N sulphuric acid mixed with 0.04M ceric ammonium sulphate also in 1N sulphuric acid. The indicator was 1 : 10 phenanthroline (Red - Blue); the working voltage, 0.75v with a reversal time of 15 seconds. A system of 0.04M both in ceric and cerous ammonium sulphate in 0.1N sulphuric acid containing Xylene Cyanol FF as indicator (Green - Orange) worked with a voltage of 1.2v, but the reverse charge was very slow (15 minutes).

To minimise diffusion effects and to also bring the cell contents nearer to textile substrates in character, the addition of gels was tried. Gels of polyvinyl alcohol, methyl cellulose, polyvinyl pyrrolidone, agar and gelatin were investigated. Polyvinyl alcohol has the added advantage in the iodine/ferrocyanide system of acting as an indicator in addition to its gel function, so this system was especially investigated. The cell had as faces two transparent electrodes, which were separated by a hollow round spacer. The working electrolyte was 0.08% iodine, 0.8% potassium iodide, enough potassium ferrocyanide to neutralise the iodine present, dissolved in a gel of 1.5% polyvinyl alcohol. The working voltage was 3v and a dark blue color was produced on the anode in 2 minutes but reversal took 4 minutes; no gas was produced if the working voltage was less than 3 volts. There is a delay in forming the blue color at the other electrode on reversal so a blue-colorless reaction is possible.

More efficient cells were however made by the use of bipyridilium compounds. A favored bipyridilium was heptyl viologen dibromide that gives a purple color. Since the dark blue color deposits on the electrode, the viologen derivatives can be used either as shutters or for color display, because colors other than blue are possible with different viologen derivatives. Unfortunately these compounds are highly toxic, and care must be exercised in their use. Polymeric viologens with redox properties were also discovered by a survey of the literature, and some of these compounds were prepared and tested in cells. A compound (I), poly N, n-butylene - 4,4' dipyridilium dibromide was prepared. This compound is a solid and in this form was sandwiched between transparent electrodes. It is initially yellow, but changes to a deep blue on application of a voltage around 2v (according to conditions) in 5 minutes; reversal took place slowly either on standing or by the action of a reverse potential. The polymer is water soluble, and, in the form of aqueous gels, a more satisfactory performance was achieved.

In testing these compounds, more efficient cells were designed, and tests were carried out with reflected light rather than transmitted light to simulate camouflage conditions. These cell designs included one with a top tin oxide transparent electrode and a bottom electrode, either a silver - silver salt or a silver electrode. Many experiments were performed with compound (I) as the color reagent (Pale Yellow - Deep Blue) with a 5% addition of gelatin to aid gelation with and without adjuvants. An adjuvant is a redox compound that is capable of being oxidised at the anode, whilst the radical salt is being reduced at the cathode. On reversal the oxidised form of the adjuvant will be reduced at the same electrode, whilst the radical ion is oxidised at the other. Adjuvants such as ferrous ammonium sulphate, potassium ferro-cyanide, tetra chlorohydroquinone and hydroquinone were tried, but the latter was the most successful. Another adjuvant, N,N,N',N' tetramethyl-p-phenylene diamine dihydrochloride in the presence of sodium sulphite was also found to be very efficient, and in cells with compound (I) excellent operation was obtained.

The best cells so far evolved are those with a tin oxide transparent cathode and a silver anode containing compound (I), gelatin or agar, hydroquinone or other adjuvants, with and without potassium bromide. Such cells work in a voltage range of 1.0 - 2.0 volts and operate in less than 1 minute in either direction. All cells have to be degassed and purged with nitrogen before use to eliminate residual oxygen.

Several display cells illustrating these principles have been produced. It was found that colored pigments could be included in the cell contents, so that any color could be displayed or cut-off as required. Suitable pigments were found for all colors in the Acramin (Bayer AG) range of pigments. Clearly by correct juxtaposition of different colored cells, an effective camouflage display could be achieved, which could be changed in design of color by suitable electrical connections. The application of such principles to textiles therefore requires future attention to make the concept viable in practical terms.

The alternative method of the use of redox systems is to obtain color transformation by the cell contents under the influence of an applied potential. If viologens were to be used in this system, then it becomes necessary to find those that have the necessary color reactions. Heptyl viologen gives a colorless - purple change. A pale yellow to red change was found with 6,7, dihydro-13-oxo-13H-dipyrido (1,2-d: 2', 1'-g) (1,4) diazepinedi-ium dibromide (compound (III)), but the color reactions appeared only to be easily produced in dilute concentrations. Cells containing compound (III) were also constructed with added pigment to give other color changes; for example, a green pigment gave a green-brown change as a result of the combination of the color change of the compound B and the green of the pigment.

Electrochemical color reactions were also observed with anthraquinone derivatives. The best one so far encountered was the sodium salt of 2:6 anthraquinone disulphonic acid (compound (IV)). Cells containing compound (IV), and potassium ferrocyanide in a gelatin gel, operated successfully with a tin oxide transparent cathode and a silver anode; the color change was pale yellow to a dark red. Work with solvents other than water is in a very early stage, but it has been observed that anthraquinone in dimethyl formamide changes from pale yellow to red under suitable conditions. The use of solvents other than water is necessary if electrochemical changes are to be observed at very low temperatures, as found in some environments where camouflage may be required. The pursuance of these aspects of the problem, however, cannot be undertaken in the present stage, but must be left to future development.

Conclusions

The work has shown clearly that the use of electrochromic color display for camouflage purposes is feasible, but much development work is required to take practical advantage of the principles discovered.

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INTRODUCTION

The main objective of the research arose from the need for combat clothing with reflectance properties that can be controllably and rapidly altered to match various terrain backgrounds. The general principles to be used in meeting this objective have been set out in the Specification, and the present research was designed to implement these general principles.

In the proposals put forward to implement the Specification the study of the following systems was proposed as a basis on which to start work:

- (i) A study of the redox properties of dyes.
- (ii) A study of the masking of colored substrates by filters with reversible properties.

During the course of the research the systems were primarily studied in cells or other appropriate apparatus, so that a background of relevant data could be accumulated. From these data the necessary factors for application to textiles were expected to emerge. Naturally, any direct approach to textile application was studied whenever this became evident during the research.

As a background to the research was the principle that any color can be produced to an observer at a distance by the correct pattern of colored areas of three primary colors, which for additive color processes are green, cyan (blue) and magenta (red). If therefore the display of three colors can be masked or displayed by electrical methods the observed pattern of color can be changed. The actual pattern displayed will depend on the pattern of the electrical connections to the numerous cells making up the display, and this will be conditioned by the nature of the camouflage required. If necessary subtractive color principles can also be used when the primaries then become the well known red, yellow and blue, but basically the same electrical principles will still be used.

MASKING OF COLOR

Introduction

In this section of the work the objective was to find shutter systems to mask or display color by electrical methods. The initial attempts were with the Kerr electro-optical effect.

The principle of the Kerr effect is that suitable liquids placed in an electrical field behave optically like uniaxial crystals with the optic axis parallel to the field direction. Plane polarized light passed through such a system becomes elliptically or circularly polarized and is therefore not blocked by a second polarizer crossed with the first. Thus whilst the electrical field is operative, light passes through the system and does not (due to the crossed polars) when the field is turned off. For countersurveillance purposes the system must operate with reflected light and this can easily be arranged by a combination of a colored polarizing screen and a quarter wave plate placed in front of a Kerr cell, and the cell backed by a highly reflecting surface.

Development of the Kerr-cell application

On consideration of the Kerr cell as a shutter it became evident that the electric field should be perpendicular to the transmitted light. As a result the cells have to be long and narrow for the effect to be observed with relatively low voltages. The magnitude of the effect is governed by the Kerr constant of the liquid used in the cell. One of the best liquids known is nitrobenzene with a Kerr constant of $j = 2.44 \times 10^{-12} \text{ m}^2 \text{ V}^{-2}$. The equation relating the optical path difference with the dimensions of the cell is:

$$\Delta = j \frac{1 E^2 \lambda}{d^2} \quad *$$

where Δ = path difference (λ)
l = electrode length (metres)
d = electrode separation (metres)
E = applied voltage (volts)
 λ = wavelength of light

Two basic systems can be set up as shown in Figures 1 and 2. The transmission system shown in Figure 1 is useful to demonstrate the effect, but for countersurveillance purposes the system shown in Figure 2 needs to be used. On the operation of the voltage a total path difference in the cell of $\lambda/2$ is required, which is provided by a double passage through the cell in the reflection system; i.e., the cell itself must provide a path difference of $\lambda/4$ in this system. If this optical path difference is given, then light will pass, although the polars in the transmission system are crossed. In the reflection system what is effectively crossed polars is provided by a polarizer, a $\lambda/4$ plate correctly oriented and a suitable reflecting surface.

*(1) Jenkins & White 'Fundamentals of Optics' p.604. McGraw-Hill, N.Y.
Other references (2) - (4)

Thus, for an optical path difference of $\lambda/4$, to operate the reflection system with a Kerr cell 40 mm long and an electrode separation of 0.1 mm filled with nitrobenzene, the required voltage is:

$$E^2 = \frac{10^{-8}}{4 \times 2.44 \times 10^{-12} \times 4 \times 10^{-2}}$$

$$E = 160 \text{ Volts}$$

To reduce this voltage or to have cells with more convenient dimensions requires the discovery of a liquid (or solid) with a Kerr constant at least 5 times that of nitrobenzene. Such a liquid has as yet not been discovered, as far as can be ascertained.

Early experiments were conducted with the transmission system, since this was the easiest system with which to demonstrate the effect. The original cells were constructed from brass plates separated by polyethylene spacers and held between microscope slides. Once the effect had been demonstrated, more refined cells were constructed. One successful cell was made with stainless steel electrodes 40 mm long and 20 mm wide separated 0.1 mm with PTFE (polytetrafluorethylene) spacers held in a silica cell with polished silica ends. The operating voltage of such a cell was expected to be around 150-200 volts. The optimum light transmission was observed with 200-250 volts.

In the early experiments with this cell it was found that the effect decreased with the duration of the application of the voltage. At the same time the liquid within the cell was seen to move vigorously during the application of the voltage. These effects were traced to impure nitrobenzene. Electrical breakdown occurred with this nitrobenzene at 300 volts.

The nitrobenzene was purified by leaving it in contact with Amberlite Monobed Resin MB-1 which had first been treated with 1,4-dioxan. No significant improvement was found after 24 hours, but after 14 days' treatment the resistivity of the nitrobenzene was found to be improved. This purified nitrobenzene gave markedly increased light transmission at a given voltage, and the liquid agitation was reduced. Furthermore no ageing effect was observed during the operation of the cell over periods greater than one hour. However if the nitrobenzene was left exposed to the air for several days, the ageing phenomenon returned.

The length and size of cells so far discussed were of no value for the objective of camouflage, especially if applied to clothing, so that it was relevant to make a few simplified calculations to see whether practical cells were feasible. For a path difference of $\lambda/2$ equation (1) can be written:

$$\left(\frac{E}{d}\right)^2 = \frac{1}{2jl}$$

Moreover, if j for nitrobenzene is taken as $2.5 \times 10^{-12} \text{ mV}^{-2}$ to simplify calculations, the equation reduces to:

$$\left(\frac{E}{d}\right)^2 = \frac{2 \times 10^{11}}{1} \quad (2)$$

For a reasonable viewing angle it is at least desirable to have the length of the cell equal to the separation of the electrodes. Such a cell to work on (say) 50 volts would therefore require the dimensions given by:

$$\frac{2500}{1^2} = \frac{2 \times 10^{11}}{1} \quad (\text{for } l = d)$$

$$\text{or } l = d = 12.5 \text{ mm}$$

which is clearly impractical. Even if such a cell could be constructed there is the added factor of the electrical breakdown of nitrobenzene under such conditions.

If a cell were constructed with an electrode separation of 0.1 cm and length 0.5 cm to work with an applied voltage of 10 volts it would require a liquid with a Kerr constant of $j = 10^{-6} \text{ mV}^{-2}$, a constant so much greater than that of nitrobenzene, that it is unlikely that such a liquid exists.

On the basis of this simplified equation (2) and for an optical path length of $\lambda/2$ it is possible to calculate various limiting working voltages. The other factor to be taken into account is the breakdown strength of nitrobenzene which here is the maximum usable field. According to Bright, Makin, and Pearmain², the value is 10^7 v/m for nitrobenzene. If these calculations are plotted, the result is as shown in Figure 3. Thus for a cell of length 10 mm with an electrode separation of 1 mm, a supply voltage of 4500 volts is required, and the field strength is below the breakdown strength of nitrobenzene (Figure 3).

These calculations thus show that for clothing where small cells would be required, the necessary voltages would be too high, and where smaller voltages may be in the feasible range, the long cells then are impractical.

The conclusion drawn is that the Kerr effect with nitrobenzene as the operative liquid may possibly be used for large objects, tanks, lorries, buildings etc., where large cells are practicable and where large voltages could be tolerated, but it cannot readily be used for clothing.

Alternative Materials

H. Pursey⁶ claimed to have observed the Kerr-type electro-optic effect with polystyrene and polymethylmethacrylate and estimated the value for the Kerr constant for the latter as 10^{-12} mV^{-2} ; i.e., about half that for nitrobenzene. Since polymethylmethacrylate can be conceived in textile application, an investigation of such solid polymers seemed worth while.

Work was conducted on films of polymethylmethacrylate and although several attempts were made to use this material in Kerr cells no Kerr electro-optic effects were observed even at high relative voltages. Thus for example a cell element of PMMA (6 x 46 x 0.42) mm even up to 800 volts failed to give any response.

Direct communication with H. Pursey elucidated the fact that the original evidence given as basis for the letter in 'Nature' was in error. The observed effects had been traced to other factors and no Kerr effect was in fact observed; unfortunately no refutation in the literature has been made. In view of this evidence it was not surprising that no effects were observed in these experiments, and therefore further work on this system was abandoned.

This work, however, drew attention to other solid systems, and in particular to the hot pressed PLZT (Pb, La, Zr, Ti) O_3 ferroelectric ceramics.⁷⁻¹¹ Attempts have been made to obtain some of this material without success. As far as can be ascertained the high operating voltages required probably will discount this material for the present objective, but its potential use must not be overlooked.

ELECTROMAGNETIC SHUTTERS

The principle employed in this section was that needle or plate-like particles lying adjacent to one another cause an obstruction to light. If these particles are aligned on end parallel to the path of light, then a high percentage of the light will be transmitted. The alignment of magnetic particles is perfectly feasible in this way by the operation of an electro-magnet, and the work was directed to finding the simplest system of particles with the minimum size of solenoid to operate it.

The initial experiments were carried out with a suspension of iron particles in liquid paraffin in an apparatus depicted in Figure 4. As might be expected, particles with roughly equal dimensions in the three directions at right angles were found to be ineffective in causing a light transmission difference (LTD) with or without a magnetic field. Needle-shaped and disc-shaped particles were found to have a much larger effect on LTD. Two groups of iron particles were tried (i) > 300 mesh (53M), (ii) < 300 mesh, but both had large proportions of symmetrical particles which considerably reduced the LTD.

Further experiments were conducted with particles of magnetic iron oxide, which was available as a fine powder. It was found that:

- (1) On the application of a magnetic field, the very small iron oxide particles joined to produce long needle-shaped particles along the direction of the magnetic field.
- (2) A very high LTD was obtained with these needle-shaped particles.
- (3) Only when the magnetic field is exactly along the viewing axis is the optimum LTD achieved. Reference to Figure 5 shows the expected magnetic field in the cell, and the particles in lining up with the lines of force will achieve only partial orientation at the outside of the cell.
- (4) On the removal of the magnetic field low light transmission was achieved by the movement of the particles under gravity. This took place in periods up to 5 sec.
- (5) To speed up the extinction, a second solenoid was introduced at 90° to the first. As the voltage was switched from one solenoid to the other, so the particles became aligned along the horizontal field lines, and the minimum light transmission was considerably increased.

These observations were made with a horizontal cell so a simple vertical cell as illustrated in Figure 6 was made to observe the conditions with this cell. A mixture of magnetic oxide particles in liquid paraffin was introduced into the cell, and their behavior, studied when a current was supplied to the solenoid. The performance was very similar to that with the same cell in the horizontal plane, except that the particles drifted slowly to the bottom of the cell over a period of some minutes. Re-dispersion of the particles by simple ultrasonic or thermal agitation was unsuccessful.

To make cells of this type viable, it may be necessary to anchor strips of magnetic material at one end, so that by the operation of a magnetic field, maximum light transmission is achieved by the strips standing virtually on end, whether the cell is horizontal or vertical. Some experiments of this nature were performed, but no conclusions were reached because of the experimental difficulties of forming the cells.

The possibility of the use of highly viscous liquids may also provide some solution to some of the problems. However, the outstanding difficulty is providing a sufficiently high magnetic field with a low voltage in a small space.

Further investigation of this system was, however, suspended because of the success of experiments based on redox reactions, and experimental effort was therefore transferred to these systems, which are described in the rest of the report.

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REVERSIBLE ELECTROPLATING CELLS

The basic concept is to deposit a metal film on to a transparent electrode by an electrolytic process, thus forming a shutter; reversal of current removes the coating and opens the cell.

Early experiments were conducted with simple cells with a transparent tin oxide cathode and a silver anode, filled with silver nitrate solutions. It was discovered that the concentration of solution was important to obtain an even deposit. Thus at concentrations above 0.5 g/l, with an electrode of surface resistivity of 5K /square and an electrode separation of 2 cm, with an applied voltage of 12v and current flow of 1 mA, an uneven deposit was formed. On reversal under the same conditions the deposit was not completely removed, but no gas was evolved.

This experiment showed the feasibility of the idea, and a search of the literature revealed details of a more workable cell. According to S. Zaromb¹, a cell of parallel closely spaced flat narrow transparent electrodes with line symmetrically placed contacts should work satisfactorily if filled with the solution:

$\frac{M}{100}$	silver iodide	} in 10 ml of solution
$\frac{M}{100}$	sodium hydroxide	
$\frac{5M}{100}$	sodium iodide	

Cells of this type were tested it was found that:

- (a) The switching times were of the order of less than 1 second, with a voltage range around 3 volts.
- (b) Deplating took longer than the initial plating.
- (c) Repeated switching caused some of the deposited silver to flake off and deposit on the bottom of the cell.

However, it was concluded that the system could be developed, and finally color, added to make it a possible alternative to straightforward redox systems.

An improved cell was first constructed to the design shown in Figure 7. The Baltracon coated glass has a sheet resistance of 100 ohms/square and good light transmission. A suitable circuit for studying the action of this cell is shown in Figure 8. The same solution as just described was used to fill the cell.

In operation, the capacitor C is charged to the right voltage by depressing the push-to-make switch S1. Switch S2 is a double-pole change-over switch with a centre off position enabling the capacitor C to be discharged through the cell. S2 also allows the polarity of the voltage applied to be reversed. With the optically transparent electrode (OTE) negative with respect to the second electrode, the OTE becomes plated, and reversing the polarity deplates the cell. The voltage applied to the cell is also applied to one trace of the oscilloscope and triggers the oscilloscope sweep, thus allowing the decay of the capacitor voltage through the cell to be observed. Light from a 6V, 15W bulb is passed through the cell and falls on the active area of a phototransistor. The phototransistor is connected to a second transistor to form a Darlington-pair. This arrangement allows the change in transmitted light intensity to be observed on the second trace of the oscilloscope.

The charge Q, stored by a capacitor of C Farads, charged to a voltage V volts is given by:

$$Q = CV \text{ coulombs.}$$

Thus the plating charge can be varied by varying the voltage V, or by varying the value of the capacitor C. The cell represents a resistance, through which the charge on the capacitor C leaks away, at a rate determined by the resistance value of the cell as follows:

$$V = V_0 \exp(-t/\tau)$$

where V_0 is the capacitor voltage, V the voltage at time t after connecting the capacitor to the cell, and τ is a time-constant given by the product of the capacitance and the cell resistance. Therefore by observing the time for the voltage to fall to half its initial value ($= t_{1/2}$) the resistance of the cell can be determined.

$$\tau = CR = 1.44 t_{1/2}$$

$$\therefore R = 1.44 t_{1/2}/C \quad t \text{ in seconds, } C \text{ in Farads.}$$

With this system and the cell described above it was found that the cell resistance was approximately 60 ohms. With a value of C of 5000 F and an applied voltage of 10 volts the cell transmission after plating was almost zero. The transition from transparent to opaque took approximately 200 m sec and there is a delay of approximately 20 m sec after applying the voltage, before the optical transmission begins to change. There were several problems associated with this cell. Firstly, the electrolyte tended to leak away due to imperfect sealing of the cell, and secondly, the plating was not uniform. The finite resistance of the Baltracon coating meant that a portion of the applied voltage was dropped across the electrode, between the metal contact and the aperture. Thus the metal tended to deposit on the edge of the aperture nearest to the metal contact.

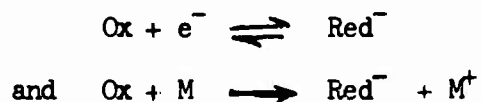
To overcome these problems a second cell was constructed. This cell had the same construction as the previous one (Figure 7), but the rubber gaskey was replaced by glass, giving a cell 2 mm thick with an aperture width of 2 mm. To improve the plating uniformity, the Baltracon layer was covered with a layer of gold, deposited by vacuum evaporation and condensation, except in the region of the aperture. The resistance of this cell was found to be approximately 20 . With a value of C of 5000 F, it was found that a voltage of 2V was required to produce a detectable change in transmitted light intensity, while voltages greater than 4 volts gave complete opacity. Higher voltages also showed faster plating times.

At this stage it was found that the photodetector had been saturated in the above experiments, and so small changes in transmitted light intensity were not detected. The photodetector was found to saturate at an output voltage of 7 volts, and so the light intensity, with the unplated cell in position, was adjusted to give an output of 6 volts from the detector, and the optical transmission values quoted below are expressed as a percentage of the light transmission through the unplated cell.

Figure 9 shows a typical curve of transmission as a function of applied voltage. It can be seen that for a given voltage, greater opacity was obtained with increasing values of C, consistent with the fact that greater C gives greater plating charge for a fixed voltage.

The cell can be deplated by applying a reverse voltage pulse. If the deplating pulse is applied within less than a second of the plating pulse, then the transmission returns to approximately 90% of the original unplated value. The original transmission can be obtained by applying a second pulse. If, however, the cell is left in the plated condition for a period of time, then application of a reverse voltage pulse does not clear the electrode. In these cases several reverse voltage pulses must be applied before clearing of the cell results. Alternatively, a higher voltage may be used when fewer pulses are required.

Deplating of the cell occurs by the following mechanism:



where Red^- is the reduced form of Ox and M is the plated metal. For example, in the basic solution used here the Ox component is IO_3^- . The Ox component is formed in the solution at the plated electrode. The Ox component is then free to diffuse away from the plated electrode, and obviously, the longer the time after the plating pulse, the greater will be the effect of this diffusion, and so less and less Ox component will be present at the plated electrode. It should be possible to minimize this effect by passing a small constant current, subsequent to the initial plating pulse, to prevent the diffusion of the Ox component away from the electrode.

To overcome the difficulties, it was decided that the capacitor discharge system for plating and deplating the cells should be replaced by a pulse generator. The heart of the pulse generator is a timer integrated circuit, designated Timer A, available from R. S. Components Ltd. Timer A is a silicon monolithic timing circuit that can be used to give one shot or a stable operation and is similar to the NE555V, MCL455P or LM555CN offered by other manufacturers. Timer A comes in an eight pin DIL package, and the pin configuration and a block diagram of the circuit are shown in Figure 10. The timer circuit was used in the one-shot (monostable) mode using the manufacturer's recommended circuit shown in Figure 11. The circuit gives a single pulse, the length of which is given by:

$$T = 1.1 \times R_1 \times C_1$$

where C_1 is in Farads, R_1 is in Ohms and T is in seconds.

The maximum value of R_1 for reliable operation is determined by the value of the threshold current (I_T) into pin 6 which is $0.25 \mu A$ (MAX).

$$R_1(\text{MAX}) \leq \frac{V_{CC}}{3 \times 0.25} \text{ M}\Omega$$

i.e. for 15V operation $R_1(\text{MAX}) = 20 \text{ M}\Omega$. Ideally R_1 should be kept as small as possible. C_1 is determined from the formula for the time delay. The values actually used in the circuit were: $R_1 = 1.1 \text{ M}\Omega$; $C_1 = 1 \mu F$. R_1 is, in fact, a $1 \text{ M}\Omega$ linear potentiometer in series with a fixed $100 \text{ K}\Omega$ resistor, enabling the pulse width to be varied from approximately 0.1 sec to 1.2 sec. The pulse height, in volts, is determined by the supply voltage and in fact varies slightly with load current. The pulse time also varies slightly with supply voltage, and so, to have a range of output voltages, the following arrangement was used:

The load in Figure 12 is the operating coil, type 1 from R. S. components, for a dry-reed switch, type 13-RSR-H again from R. S. components. For the duration of the pulse, generated by the timer, the reed operating coil is energised causing the reed switch contacts to close. The reed switch is used to apply the output of a variable voltage D. C. power supply (Weir Minireg Power Supply type 401-1) to the electrolyte cell as shown in Figure 13. The double-pole, double-throw switch in Figure 12 allows the polarity of the output pulse to be changed for plating and deplating the cell. The power for the timer circuit was derived from the A. C. mains, via a small transformer and an integrated circuit voltage regulator, the circuit for which is shown in Figure 13. The pulse generator, described above, was thus capable of supplying output pulses from 0.1 seconds to 1.2 seconds long with the pulse voltage variable from 0 to 20V at up to 1 ampere.

Experiments were carried out on a cell similar in construction to the one described previously (Figure 7). A diagram of the cell and its dimensions is given in Figure 14. The alkaline electrolyte described previously was again used; i.e., 1M AgI plus 1M NaOH in 5M NaI solution. Figure 15 shows a current-voltage characteristic for the cell. The current was measured with an AVO Model 8 multimeter, with 1 second pulses applied to the cell, and allowance was made for the voltage drop across the meter. Up to applied voltages of approximately 1 volt the curves exhibited ohmic behaviour, and the cell resistance was seen to be approximately 22.5Ω . Above 2 volts the current through the cell became proportional to $V^{1.5}$; i.e., indicative of a space-charge limited current. As the voltage across the cell was increased, the deplating current could also be seen to be less than the plating current at a given voltage. This effect helped to explain the fact that a single deplating pulse, equal in voltage and pulse width to the plating pulse, was usually insufficient to completely deplate the cell. The deplating pulse in the above experiment was applied within 3 or 4 seconds of the plating pulse. Figure 16 shows the light transmitted through the cell, as a percentage of the light transmitted in the unplated condition, as a function of applied voltage and pulse width. As expected, the transmission through the cell decreased with increasing voltage and pulse width.

It is instructive at this point to look at some of the theory underlying the design of an electroplating light modulator. A parameter for comparing different platable metals may be derived as follows (S. Zaromb¹): The absorption coefficient, as defined by the Lambert equation:

$$I_t = I_i e^{-\alpha \theta} \quad (1)$$

where I_i is the intensity of the incident light and I_t the intensity transmitted through a thickness θ of a given metal, is related to the wavelength, the absorption index K , and the index of refraction n by the equation (F. Seitz²):

$$\alpha = \frac{4\pi nK}{\lambda} \quad (2)$$

The thickness θ of electrodeposited metal for a plating charge density Qd (in coulombs/cm²) depends on its atomic weight W , density d , oxidation state Z of the platable ions, and the plating current efficiency in this relationship;

$$\frac{\theta}{Qd} = \frac{EW}{ZFd} \quad (3)$$

where F is the Faraday unit. Hence the optical density change due to plating, as defined by the equation,

$$\frac{I_t}{I_i} = 10^{-\delta} \quad (4)$$

should be, according to equations (1) to (4),

$$\delta = \frac{4\pi nKQ d EW}{2.303 \lambda FZd} = \log_{10} \left(\frac{I_i}{I_t} \right) \quad (5)$$

i.e., δ is the logarithm of the ratio of incident to transmitted light intensity.

If it is assumed that ϵ be 100%, the expected change in optical density per plating charge density becomes:

$$\frac{\delta}{Qd} = 5.65 \times 10^{-5} \text{ nKW} \quad (6)$$

The ratio $\text{nKW}/(\lambda ZD)$ thus gives a relative parameter for comparing the minimum charge density requirements with various platable metals. Table 1 lists values of δ/Qd for various metals for wavelengths in the visible region³.

The highest values of δ/Qd may be expected for Se with $\lambda < 0.49\mu$, for Ag with $\lambda > 0.395\mu$, for Sn with $\lambda = 0.589\mu$ and Cd with $\lambda = 0.589\mu$, and these would seem to be the best metals to use, especially in view of the fact that silver is known to work well. However, too much reliance should not be placed on the values of δ/Qd for the following reasons. The values of the parameters used to calculate δ/Qd are for bulk specimens of the metals. It is well known that thin films of evaporated or sputtered metals have values of n and K vastly different from the bulk values.^{4, 5, 6, 7}

With most metals the light transmission falls to less than 1% for film thicknesses greater than a few hundred Angstrom units, and the reflection reaches a plateau at similar values of thickness. Thus films of this order of thickness (say 200 Å) are needed in the present work and it must be assumed that the optical constants of electrodeposited films are different from those of bulk specimens of the metals. Furthermore, the experimental values of optical constants obtained by several workers are not in sufficiently good agreement to be considered reliable.

Table 1. Estimated optical density change per plating charge density for various elements and wavelengths

Element	d(gm/cm)	Z	W	$\lambda(\mu m)$	nK	δ/Qd
Cd	8.64	2	112.4	0.589	5.01	31.3
Cr	7.3	3	52	0.579	4.85	11.4
Co	8.9	2	58.9	0.500	3.72	14.0
Co				0.650	4.40	12.7
Cu	8.92	2	63.6	0.347	1.47	8.5
				0.500	2.34	9.4
				0.650	3.26	10.1
				0.870	3.85	8.9
Au	19.3	1	197	0.441	1.85	24.2
				0.589	2.83	27.6
I	4.93	-1	126.9	0.589	0.57	14.1
Ir	22.4	4	193.1	0.579	4.87	10.2
Pb	11.3	2	207.2	0.589	3.48	30.6
Mn	7.2	2	54.9	0.579	3.89	14.5
Ni	8.9	2	58.7	0.420	2.53	11.2
Ni				0.589	3.33	10.5
Ni				0.750	4.36	10.8
Pt	21.5	2	195.2	0.441	3.16	18.4
Pt				0.589	3.54	15.4
Pt				0.668	3.66	14.1
Rh	12.4	3	102.9	0.579	4.67	12.6
Se	4.8	2	79	0.400	6.79	79.0
Se				0.490	4.65	44.1
Se				0.589	1.32	10.4
Se				0.760	0.156	0.95
Ag	10.5	1	107.9	0.332	0.65	11.4
Ag				0.395	1.91	28.1
Ag				0.500	2.94	34.2
Ag				0.589	3.64	35.9
Ag				0.750	5.16	40.1
Sn	7.28	2	118.7	0.589	5.25	41.1

Table 1. (continued)

Element	d(gm/cm)	Z	W	λ (μ m)	nK	δ/Qd
Zn	7.14	2	65.4	0.441	3.19	18.7
Zn				0.589	4.66	20.5
Zn				0.668	5.08	19.7
Al	2.7	3	27	0.589	5.32	17.0
Fe ~	7.5	2, 3	55.9	0.589	2.46	8.8 (Z=2)
Mg	1.74	2	24.3	0.589	4.42	29.6
Ta	16.6	5	180.9	0.579	2.31	4.91
W ~	19	6	183.5	0.579	2.7	4.25
W				0.589	3.25	5.03
V ~	6	5	50.95	0.579	3.51	5.8

This is probably due to differences in the mode of film deposition, since the theory due to Maxwell Garnett and developed by Schopper clearly shows now the apparent optical constants depend upon the structure of the film and on a parameter g , which is a measure of the fractional volume occupied by the metal in the film. Hence, the only conclusion which can be drawn from previous thin-film studies is that any quantitative predictions based on Table 1 may be in error by as much as a factor of 2 or 3 for plated film thicknesses of less than 200 Å. So it would seem reasonable to continue to use electrolytes based on silver as the platable metal, bearing in mind that other metals could be investigated later if necessary.

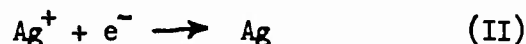
One of the main problems with the electroplating cell is the achievement of uniform plating over a large enough area. This problem divides into two parts. Firstly there is the effect of the plating solution. For 100% over-all plating current efficiency, the most serious deviation from the minimum charge requirements estimated in Table 10 may arise from a non-uniform plating density. This is a common problem in electroplating, and most industrial plating solutions have the property of 'smoothing out' the plating density, even over somewhat irregularly-shaped substrates. Unfortunately, most industrial plating solutions contain unstable and/or highly toxic agents (e.g. cyanides) which are unsuitable for our application.

The mechanism by which a plating solution tends to counteract the effect of geometric irregularities appears to be associated with an overpotential rapidly increasing with current density^{10, 11}. Negative complexing ions usually increase the overpotential by transforming readily platable cations into less readily platable anion complexes. Thus, silver plating solutions have been recommended based on fluoborate,¹² rhodanide¹³, thiosulphate¹⁴, and iodide complexes.¹⁵ The last appear especially suitable for reversible electroplating cells.

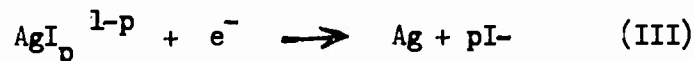
The mechanism by which silver is plated from concentrated iodide solutions cannot occur via the steps,



followed by,



because the concentration of free Ag^+ ions in 5 to 10M iodide solutions cannot appreciably exceed 10^{-17}M (the solubility product of AgI being 8.5×10^{-17}). Although the concentration of dissolved AgI molecules or $\text{AgI} \cdot \text{H}_2\text{O}$ molecular complexes should be more appreciable in view of the ease of precipitation of AgI from 1M iodide solution, it still cannot exceed 10^{-6}M . Hence, the most likely mechanism must be of the form,



where p may be a value between 2 and 4¹⁶. The negatively charged AgI_p^{1-p} species approaching the cathode must proceed under the influence of a concentration gradient against the direction of the applied electric field. Hence, for continuous plating at high current densities, reaction (III) should be diffusion-controlled, and the current density i_c approaches an asymptotic limiting value i_L with increasing overvoltage in this relationship,

$$i_c = i_L (1 - e^{zFn/RT}) \quad (7)$$

where i_L depends mainly on the concentration of the platable complex and on thickness of the stationary layer of electrolyte adjacent to the cathode. 11,17 Reported polarization curves for a solution of 0.01M AgI_2^- in 1M KI (A. Zeven¹⁰) with different stirring rates actually show the asymptotic variation of i_c predicted by equation (7). A similar asymptotic behaviour or plateau in the i_c vs n plot appears likely with more concentrated solutions. However, the plateau could hardly extend over a range of more than a few tenths of a volt before the occurrence of hydrogen evolution. Although the latter may not affect the uniformity of the plating, it would lower the current efficiency just the same. Thus, the use of a suitable plating solution and of an optimum plating rate may, at best, allow for geometric voltage drop irregularities amounting to no more than a few tenths of a volt.

In view of the expected limited effectiveness of even the best possible plating compositions, special attention must be given to the geometric requirements for uniform plating density. In the reversible electroplating cell, as well as in other devices or experiments involving reactions at semiconducting or even very thin metallic electrodes, the current density distribution may be seriously affected by ohmic potential drops along the electrode surface. The conditions for maintaining essentially uniform current densities in spite of non-uniform surface potential may be established for several cell configurations.

Perfectly Uniform Parallel Current Flow Lines in the Electrolyte

Let J_x be the current density in the electrolyte along the x -direction perpendicular to the surface of a rectangular (highly conducting) metal electrode M . The shape of a surface-conductive glass electrode g (Figure 17) required for J_x to be uniform will now be determined. Let x and y be the horizontal and vertical coordinates of any point P on the curve S_g defining the glass surface. The surface current I_g flowing along the glass surface toward the collector strip C (outside the cell) is then given by,

$$I_g = L \int_0^y J_x dy \quad (8)$$

where L is the length of the cell along the direction perpendicular to the plane of Figure 17. The difference in potential between points $P_1(x, y)$ and $P_2(x + dx, y + dy)$ on the curve S_g then becomes,

$$-dV_g = (I_g/L) \rho_g dS_g \quad (9)$$

$$\begin{aligned} &= \rho_g \left(\int_0^y J_x dy \right) dS_g \\ &= \rho_g J_{xy} dS_g \end{aligned} \quad (9^1)$$

where ρ_g is the surface resistivity of the glass. On the other hand, assuming no change in overvoltage between points P_1 and P_2 ; i.e., essentially uniform current density, dV_g may be readily calculated by following a path through the electrolyte using the equation,

$$-dV_g = J x \rho_e dx \quad (10)$$

where ρ_e is the volume resistivity of the electrolyte, Equations (9¹) and (10) combine to give,

$$\frac{dS_g}{dx} = \frac{\rho_e}{\rho_g y} \quad (11)$$

but for any curve

$$\frac{dS_g}{dx} = \left[1 + \left(\frac{dy}{dx} \right)^2 \right]^{1/2} \quad (12)$$

Therefore,

$$\frac{dy}{dx} = \frac{\rho_e}{\rho_g} \left[\frac{1}{y^2} - \frac{\rho_g^2}{\rho_e^2} \right]^{1/2} \quad (13)$$

$$= (k^2 - y^2)^{1/2} / y \quad (13^1)$$

where

$$k = \rho_e / \rho_g \quad (14)$$

Rewriting,

$$(13^1) \quad dx = ydy/(k^2 - y^2)^{1/2} = -d(k^2 - y^2)^{1/2} \quad (15)$$

it can be shown,

$$x = \left\{ k \left[1 - 1 - (y/k)^2 \right]^{1/2} \right\} \quad (16)$$

Equation (16) is plotted in Figure 18.

For the condition $y \ll k$ (17)

Equation (16) reduces to

$$x \approx y^2/2k \quad (18)$$

$$\text{and } x \ll y \quad (19)$$

i.e., the electrode g is almost parallel to M , and the actual current density on the glass surface is equated as,

$$i_g = Jx \frac{dy}{dS_g} \quad (20)$$

which according to equations (11) and (15) is

$$i_g = Jx \left[1 - (y/k)^2 \right]^{1/2} \quad (21)$$

and becomes approximately uniform for condition (17); i.e.,

$$i_g \approx Jx \quad (22)$$

Table 2 shows that equations (18) and (22) deviate by less than 10% for y/k up to 0.6 and by less than 8% for values of y/k up to 0.4.

Table 2 Numerical comparisons of Equations (16), (18), (21), & (22)

y/k	$(21) / (22)$ $\sqrt{1 - y^2/k^2}$	(16) $x/k = 1 - \sqrt{y^2/k^2}$	(18) $y^2/2k^2$	$\frac{(16) - (18)}{(16)}$ $\frac{x/k - y^2/2k^2}{x/k}$
0.01		5×10^{-5}	5×10^{-5}	0
0.1	0.995	5×10^{-3}	5×10^{-3}	0
0.2	0.98	0.02	0.02	0
0.3	0.954	0.046	0.045	0.02

Table 2 (Continued) Numerical comparisons of Equations (16), (18), (21), & (22)

y/k	(21) / (22)	(16)	(18)	(16) - (18) (16)
	$\frac{1}{\sqrt{1 - y^2/k^2}}$	$x/k = 1 - \sqrt{y^2/k^2}$	$y^2/2k^2$	$\frac{x/k - y^2/2k^2}{x/k}$
0.4	0.915	0.085	0.08	0.06
0.5	0.864	0.136	0.125	0.08
0.6	0.80	0.20	0.18	0.10
0.8	0.60	0.40	0.32	0.20
0.9	0.436	0.564	0.405	0.29
0.95	0.320	0.68	0.449	0.30
1.0		1.0	0.5	0.50

The range for which J_x can be constant is, therefore, $0 \leq y/k \leq 1$ according to equation (16), while the range of fairly uniform electrode current density [equation (22)] is $0 \leq y/k \leq 0.4$ for a uniformity of $\pm 4\%$, and $0 \leq y/k \leq 0.6$ for a uniformity of $\pm 10\%$.

The above calculations show that the usable width of aperture for a given electrolyte and transparent electrode combination is limited. The Baltracon coated glass used to make the cells has a surface resistivity of 10^{-11} ohm/square, while the electrolyte volume resistivity is 10^{-10} ohm-cm. The value of $k = \rho_o/\rho_g$ is therefore 1.25mm and this value represents the maximum usable shutter width, while the width should be kept ≤ 0.5 mm to maintain a reasonably uniform electrode current density. It would seem, therefore, that to realize a large area of shutter the following approaches can be used:

- (a) The use of multiple-cell systems.
- (b) The use of transparent electrodes with higher conductivity.
- (c) The use of electrolytes with low conductivity.

(a) Multiple-cell systems

Multiple-cell systems have been discussed by Zaromb¹ but no work has been done on this at present. Multiple cell systems based upon a cylindrical cell arrangement would seem to be of particular interest to the present work since these should be easily adaptable to a textile end-use.

(b) Transparent electrodes (see Appendix)

(c) Electrolytes with low conductivity

Reducing the conductivity of the electrolyte solution will have similar effects to increasing the conductivity of the transparent electrodes, i.e., it increases the value of $k = \rho_e / \rho_g$ which controls the width of the shutter area in the cell. The conductivity of the solution is determined by the concentration of mobile charge carriers and their mobilities. Decreasing the carrier concentration will result in few platable ions being present in the solution and this will effect the performance. Making the solution into a gel should reduce the mobility of the charge carriers and hence the conductivity. The first approach tried was to add gelatin to the alkaline electrolyte solution (1M AgI + 1M NaOH in 5M NaI) which was then heated to dissolve the gelatin. Samples were made up containing up to 30% w/v gelatin. On heating all these solutions turned reddish to black in colour. The next approach was to make up a solution of 5g of gelatin in 100ml of distilled water and allow this to gel. This gel was then heated just sufficiently to liquify it and the AgI, NaI and NaOH dissolved in some of the liquid. The resulting liquid does not re-solidify but the viscosity is certainly higher than that of a solution made up with water alone.

It was decided to try this solution in a large area cell. The cell used is shown in Figure 19. The 'effective shutter width' of this cell is half the actual width (1cm) because of the highly conducting layer of silver paint which acts as the current collecting contact from the transparent electrode. Approximately 10-20% by volume of titanium dioxide was mixed in with the electrolyte. This gave a good opaque white mixture so that the effectiveness of the cell in masking a color could be observed by eye. The addition of the titanium dioxide also increased the viscososity of the solution. The plating of the cell was still uneven with the density of plating being greatest near the cell walls. However, the application of a 2 volt, 1 second pulse cause the effective area of the shutter to go from white to a dark grey color when viewed from a distance of more than 6 ft. The same effect could be obtained by applying higher voltages for shorter times. If a plating pulse was followed immediately by an equal reverse pulse, then deplating occurred near the cell walls but not in the central region.. To clear the central region another one or two reverse pulses were needed, and this resulted in a brown coloration near the cell walls; this is presumably iodine. This coloration disappeared over a period of a few minutes however. If the cell was left for a period of time in the plated state, then 4 to 5 reverse pulses were needed to clear it completely, and again the brown coloration was formed at the cell walls, which again faded in a few minutes.

Solutions with higher than 5% gelatin again showed the black precipitate. This precipitate is probably due to sulphur impurity in the gelatin and probably would not occur if a purer sample of gelatin were used. However, gelatin is reluctant to form a gel in the presence of alkali. Apart from the fact that a solid or near solid gelled electrolyte should have a low conductivity, it should also possess definite advantages from the point of view of incorporating the

reversible electroplating system into a textile or textile-like material. Consequently it was thought worth continuing along these lines and to look for another gelling agent. Polyvinyl alcohol was the next material tried. This does not dissolve very well in water (tends to go lumpy), and so a solution of 20g of P.V.A. dissolved in a mixture of 200ml ethanol and 200 ml water was made, and the ethanol was then boiled off leaving a solution of P.V.A. in water. Then 0.4g of NaOH, 2.35g of AgI and 7.5g NaI were dissolved in the hot P.V.A. solution, and the volume, made up to 10ml; i.e., the same concentration of the three salts as used in all previous experiments. The ingredients dissolved in the hot solution without any of the black precipitate found with gelatin being formed. On cooling, this solution again shows no tendency to gel, whereas the P.V.A. solution alone went quite solid on cooling. On mixing this solution with titanium dioxide, the solution was tested in the cell of Figure 19. The performance of this electrolyte was very similar to the solution with 5% gelatin described above, except that the coating was perhaps not quite as even.

Thus, although the presence of gelatin and P.V.A. had no adverse effects on the performance of a cell with an alkaline electrolyte containing these materials, they did not have the desired effect of producing a solid or semi-solid electrolyte. It seems that P.V.A. also does not gel in alkaline solution, and so a solution was made up in a P.V.A. solution as previously but omitting the NaOH. On cooling, quite a viscous solution resulted; the viscosity has not been measured but the consistency of the solution was about that of golden syrup. This solution was also tried on the cell of Figure 19, with titanium dioxide added. This solution gave the most even plating so far, and after the application of a 6 volt, 1 second pulse to this cell the shutter area appeared dark gray. On applying a deplating pulse, the cell deplated on the application of 2 - 3 pulses, if the deplating pulse followed the plating pulse within a few seconds. In this case the brown color of iodine was seen over most of the shutter area but disappeared after only a few seconds, except in the region of the electrolyte-air interface near the top of the cell. For some reason the brown coloration seemed to persist indefinitely in this region.

This neutral solution was also tried in the cell of Figure 14, and Figure 20 shows a current/voltage curve for this cell. Figure 21 shows the current voltage curve for the same neutral solution without an P.V.A. Comparison of Figures 20 and 21 shows that the P.V.A. increased the resistance of the electrolyte by a factor of approximately 6. Despite the fact that P.V.A. does not form a solid electrolyte solution it is effective in increasing the resistivity of the solution. It is also interesting to note that the resistance of the alkaline solution (of Figure 15 and Figure 21) is approximately 1.5 times that of the neutral solution. This is probably due to the formation of complex ions in the presence of excess OH^- .

CONCLUSIONS

Reversible electroplating cells have been made that function perfectly satisfactorily as shutters. They can be placed over colored areas so that these areas can be displayed or cut off as desired. The operation of the cells in both directions is less than one second and preliminary tests indicated that multiple reversibility was possible. Such cells are therefore feasible for use in camouflage if a suitable color display was arranged. However, on the advice of the Contracting Officer, Dr. A. H. Kichen, it was decided to concentrate on cells based on redox reactions, and in consequence further development of the reversible electroplating cell was left in abeyance.

Electroplating Cells

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REDOX SYSTEMS

Introduction

The provision of electrochemical shutters based on redox reactions is possible but these systems can also provide direct color changes of the desired type. Work was therefore concentrated on these systems, because not only were there alternative ways of employing redox reactions, but the voltages concerned were very small, generally less than 10 volts, and therefore perfectly feasible for the general objectives of the research.

To understand the redox systems it is necessary to redefine oxidation and reduction as the loss of electrons and reduction as the gain of electrons. Therefore, from this standpoint an oxidizing agent is one that accepts electrons and is itself reduced; a reducing agent is one that supplies electrons and is itself oxidized. Since at the anode of a cell electrons are discharged, then oxidation must take place in the vicinity of an anode, whereas correspondingly reduction must take place near the cathode that is supplying electrons.

Theoretical titration curves can be derived by the application of the equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[a_{ox}]}{[a_{red}]}$$

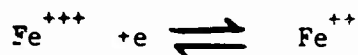
where E is the electrochemical potential, E^0 the potential of the transition point; i.e., that point at which the activity $[a_{ox}]$ balances that of $[a_{red}]$, R is the gas constant, T the absolute temperature, n is the number of electrons transferred and F the Faraday constant.

Systems with Color Changes

One method of producing color changes electrochemically is to electrically reduce or oxidize a suitable salt in solution and to follow the changes by the color reactions of selected indicators. To do this requires a knowledge of the potentials involved for each system under review and then to find a suitable redox indicator that changes color in this particular range of potentials.

The first system to be studied was the ferrous-ferric system. In this procedure, 100mls of ferrous ammonium sulphate (0.05M) was titrated with 0.05M ferric ammonium sulphate in 0.05M sulphuric acid. The potentials were measured by a platinum electrode and a saturated calomel half-cell.

Effectively the reaction is:



and the basic equation:

$$E = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

(here $n = 1$)

To convert the measured voltages found against a saturated calomel electrode to voltages on the standard hydrogen electrode scale it is necessary to add the constant.

$$\text{i.e. } V_{(\text{SCE})} + 0.2422 = V_{(\text{SHE})}$$

The results are shown in Figure 22 and in Table 3. This curve is very similar in shape to that calculated from the equation, but is displaced from it (Figure 23), because no account was taken in the calculations of activities or the ionic strength of the solutions, and no allowance made for the second electrode used (Pt).

Table 3

Potentiometric Titration of 100mls of Ferrous Ammonium Sulphate (0.05M) with Ferric Ammonium Sulphate (0.05M) in 0.05M H_2SO_4

No. of mls. of ferric ammonium sulphate added	Reading (volts) relative to S.C.E.	Voltage relative to S.H.E.
0	0.2950	0.5372
10	0.3693	0.6115
20	0.3865	0.6277
30	0.3967	0.6350
40	0.4045	0.6467
50	0.4103	0.6525
60	0.4154	0.6576
70	0.4192	0.6614
80	0.4225	0.6647
90	0.4258	0.6680
100	0.4285	0.6707
110	0.4311	0.6733
120	0.4335	0.6757

Table 4
Redox Indicators

Indicator	E at pH7 (vs S.H.E)
Methyl viologen	- 0.440
Benzyl viologen	- 0.359
Neutral Red	- 0.325
Phenosafranine	- 0.252
Methylene Blue	+ 0.011
Lauth's Violet	+ 0.063
Toylen Blue	+ 0.113
Bundschedler's Green	+ 0.224
Phenol Blue	+ 0.224
Diphenylamine	+ 0.76
Diphenylbenzidine	+ 0.76
O-Dianisidine	+ 0.80
Diphenylamine sulphonic acid	+ 0.84
Xylene cyanol FF	+ 1.05
Ferrous 1:10 phenanthroline	+ 1.06
N-Phenylanthranilic acid	+ 1.07
Ferrous 5-nitro 1:10 phenanthroline	+ 1.25
Ferrous 2 : 2' : 2'' - tripyridine	+ 1.25

To produce color changes in this system would require the addition of a redox indicator that had a color change in the range of potential over which the redox reaction took place. There are many lists of redox indicators, and a few indicators are shown in Table 4. However, if a more comprehensive list is required reference should be made to 'Indicators' by E. Bishop [Pergamon Press 1972], and other references will be found at the end of this section.

It was found that the Ferrous-Ferric system operated at voltages that were not convenient for the majority of indicators, and therefore a second single system was investigated for which a suitable indicator could be found.

The second single system to be investigated was the Cerous-Ceric system containing Xylene Cyanol FF in 0.1N sulphuric acid. The voltages measured with a calomel half cell and a platinum electrode at different concentrations of Cerous-Ceric ions are given in Table 5, and the results, plotted in Figure 24. The graph is not a smooth curve and shows a definite deviation around 1.00 to 1.05 volt. Since this is the region where the indicator changes from blue-green through orange to red, this deviation is probably the influence of the

redox system of the indicator has an influence on the main reaction. It in fact suggests that more precise results would be obtained by having two oxidation systems present at the same time. Such systems were therefore further investigated.

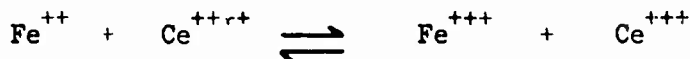
Table 5

Potentiometric Titration of Cerous acetate (0.02M) with Ceric ammonium sulphate (0.02M) both in 0.1N H_2SO_4

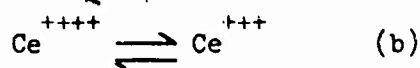
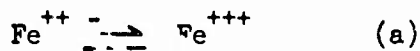
Mls of ceric soln. added to 50mls cerous soln.	Reading (volts) relative to S.C.E.	Voltage relative to S.H.E.
0	0.4755	0.7175
2	0.658	0.900
4	0.755	0.997
8	0.775	1.017
10	0.828	1.070
12	0.874	1.116
15	0.901	1.143
19	0.930	1.172
21	0.936	1.178
25	0.952	1.194
29	0.960	1.202
31	0.965	1.207
35	0.973	1.214
39	0.977	1.219
43	0.984	1.226
50	0.993	1.234
60	1.005	1.247
64	1.008	1.250
68	1.011	1.253
71	1.012	1.254
75	1.020	1.262
79	1.024	1.266
83	1.028	1.270
87	1.030	1.272
91	1.035	1.277
95	1.038	1.280
100	1.040	1.282

Systems with two simultaneous Redox Reactions

The first system of this type to be investigated was the ferrous-ferric/cerous-ceric system. The basic equation of the system is:



which can be split into two equations:



The Nernst-type equations for these systems are:

$$\begin{aligned} E &= E^{\circ} + \frac{RT}{nF} \ln \frac{[a_{\text{ox}}]}{[a_{\text{red}}]} \\ &= E^{\circ} + \frac{0.0591}{n} \log_{10} \frac{[a_{\text{ox}}]}{[a_{\text{red}}]} \end{aligned}$$

from which the theoretical calculations can be derived. In Figure 10 the lower half of the theoretical curve is derived by consideration of the equation:

$$E = E_{\circ} + \frac{0.0591}{n} \log_{10} \frac{[a_{\text{Fe}^{+++}}]}{[a_{\text{Fe}^{++}}]}$$

and the upper half by consideration of the equation:

$$E = E_{\circ} + \frac{0.0591}{n} \log_{10} \frac{[a_{\text{Ce}^{++++}}]}{[a_{\text{Ce}^{+++}}]}$$

since at the 'neutral' point all of the ferrous ions have been converted to ferric ions, and the further addition of ceric ammonium sulphate alters the potential only by the alteration of the concentrations of the ceric-cerous ions.

A practical curve is given corrected for the calomel half cell, but not for ionic strengths, activities, or the other electrode, and hence, although of similar shape to the theoretical, not of the same dimensions (Figure 25). The comparison, however, is sufficient to show which working voltages are required to drive a cell to effect either oxidation or reduction.

If to this system an indicator is added which changes in the range 0.7 - 1.2 volts, then by driving a cell through this range electrically, a colour change should be produced.

Suitable indicators for these reactions can be found with:

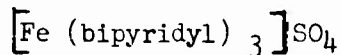
Phenanthrolines
2,2'-bipyridine complexes
Triphenylmethane dyes
Diphenylamines

amongst others, giving a possible range of color changes. Experiments were therefore set up to produce such color changes by electrically driving experimental cells containing the above ionic system plus a suitable indicator.

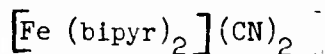
The first cells used were as shown in Figure 26, which was divided into two halves by a sintered glass disc. Equal volumes of 0.01M ferrous ammonium sulphate and 0.04M ceric ammonium sulphate in 0.1N sulphuric acid were mixed together and placed in each compartment. In the first set of experiments 1:10 phenanthroline was used as an indicator, the ferrous complex of which is red and changes to blue on oxidation. Carbon electrodes were used and 3 volts were applied to them. This voltage is in excess of that required to effect the change, and gas was formed as well as a precipitate. Lead electrodes, which have a higher overvoltage than carbon were also used, and although the change was more rapid, gas was evolved. Tin electrodes did not appear to work. In the original experiments, reversal of the change by reversal of the voltage did not work very well, and it became clear that factors other than those first suspected were operative. The importance of the nature of the electrodes was also emphasized.

Attempts to make the change occur with filter paper soaked in the appropriate solutions and electrodes laid on the wet paper showed that the potential use with textiles was possible.

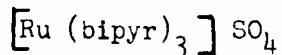
Other indicators were then tried to see what range of colors could be produced by this particular system. o-Phenanthroline acted somewhat similar to 1:10 phenanthroline but seemed slower to change, and the blue color was darker than with the first indicator. A deep red to blue change was found with 2:2' bipyridyl. Other possibilities in this range of indicators are:



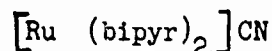
Red \longrightarrow Blue



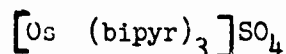
Orange \longrightarrow Pale Violet



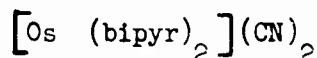
Orange \longrightarrow Green



Yellow \rightarrow Green \rightarrow Orange Brown



Green \rightarrow Pale Pink



Orange \rightarrow Pale Violet

A possible catalyst to be used with these indicators is oxalic acid.

A colourless to violet color change could be produced with:

Diphenylbenzidine

Diphenylamine

N-phenylanthranilic acid

These changes, however, were found to be unstable, and rapid decomposition set in especially when exposed to light. They are thus of little value to the particular project.

Dyestuffs also provided possible color changes in this system. To test the color changes possible, reactions were carried out by adding appropriate chemicals to the indicator solutions held in test tubes. These changes (Table 6) were effected by the use of the salts:

Ceric ammonium sulphate

Cerous acetate

Ferric ammonium sulphate

Ferrous ammonium sulphate

Stannic chloride

Stannous chloride

all in dilute sulphuric acid. These constitute possible color changes for the system under review.

Some indicators, however, were unsuccessful. o-Dianilidine which should give a change from colorless to red in the system failed to work in practice. 8-hydroxyquinoline with a change from green to yellow was found to work with carbon electrodes but the change was slow, especially in reverse. The following dyes had very little if no effect in the conditions set up.

Ferron

Methylene Blue

Phenosafranine

Safranine

Bromophenol Blue

Neutral Red

Erythrosin

Picrocarmine

Diphenylcarbazone

Crystal Violet

References to Indicators

At this point it is convenient to list the references from which information can be obtained:

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- (2) 'Colour Changes of Chemical Indicators' -III
S. Kotoly & K. Vytras Talanta 1971, Vol. 18, 253-261
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A. A. Schilt, Anal. Chem. 1963, 35, No. 11, 1599-1602
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E. Bishop & L. G. Hartshorn. Analyst 1971, 96, 26-36
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R. Belcher, J. N. Brazier, W. I. Stephen; Talanta 1965, 12, 963-965.
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N. Venkateswara Rao & V.V.S. Eswara Dutt
Z. Anal. Chem. 1971, 254, 128-129
- (7) Triphenylmethane Dyes as Redox Indicators in Dichrometry
N. Venkateswara Rao & V.V.S. Eswara Dutt
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- (8) Redox Indicators in Titrations in Aqueous Nitric Acid
S. S. Sandhu, S.C.S. Dhillon & Dula Singh
Talanta 1966, 13, 1702-1703
- (9) New Redox Systems - V. Oxidation of Uranium (IV) with Iron (III) in 1:10 Phenanthroline Solutions
F. Vydra and R. Přibil Talanta 1962, 9, 1009-1014
- (10) Vanadium (IV) 1,10 Phenanthroline Complex as a Redox Indicator
M.A. Leonard, S.A.E.F. Shahine & C. L. Wilson
Talanta 1969, 16, 470.

This list is not exhaustive.

Table 6

Dye	Ce ⁴⁺	Ce ³⁺	Fe ³⁺	Fe ²⁺	Sn ⁴⁺	
Xylene Cyanol FF	Red	Dark Blue	Green	Green	Green	Green + ppt
Victoria Blue	Chocolate ppt	Pale Blue	Green Blue	Dark Blue	Dark Blue	Blue & ppt
Night Blue	Red + Yellow	Blue & ppt	Dark Blue	Clear Blue	Dark Blue + ppt	Light Blue
Lissamine Green	Red + ppt	Clear Dark Green	Clear Dark Green	Dark Green	Yellow Green	Green Yellow
Lissamine ultra Sky Blue	Grey	Black	Purple Black	Purple Black	Black	Grey + ppt

Further Studies of Two Simultaneous Redox Reactions

A control of the reactions leading to color changes is essential, and therefore the influence of different variables on the reactions has to be understood. The mixed system represented by the equation,



was again used as basis for the study.

Variation of Reagent Concentration

The effect of varying the concentration of ferrous and ceric ammonium sulphates in 0.1N sulphuric acid on the potentiometric titration curve was first investigated. The results are shown in Figure 27, and a brief comparison, indicated in Table 7. In each experiment the concentrations of ferrous ammonium sulphate and ceric ammonium sulphate were the same, the actual concentrations being

Table 7

Vol(mls) of Ceric solution added to 50mls of Ferrous solution	Potential (against S.C.E.) for Conc. given		
	0.04M	0.08M	0.10M
0	0.2799	0.2887	0.3080
70	0.9815	1.0690	1.1758

0.04M, 0.08M and 0.10N.

It is clear that although the concentration has a significant effect on the values of the potentials, the region in which color changes take place with indicators is not greatly affected. Therefore, for color changes to take place in this system, the concentration of the reagents is not a critical factor.

Variation of Acid Concentration

The transition potential for 1:10 phenanthroline varies with the sulphuric acid concentration see (E. Bishop 'Indicators' 1972) in these systems, and it is therefore important to find how significant this change is.

In these experiments, 0.1M solutions of ferrous ammonium sulphate and ceric ammonium sulphate were used, and 1:10 phenanthroline ferrous sulphate was present as an indicator. In all these experiments the ceric ammonium sulphate solution was added by burette to the ferrous ammonium sulphate solution held in a

a beaker. The potentials quoted are those between a standard calomel electrode and a bright platinum electrode placed in a beaker. Normal potentiometric equipment was used in the measurement of the potentials. Results are presented in full on the graph (Figure 28), and an indication of the changes is tabulated in Table 8.

Table 8

Vol(mls) of Ceric (0.1M) solution added to 50mls ferrous (0.1M) soln.	Potential (U.S.C.E.) at the acid Conc. given						
	0.10N	0.25N	0.50N	1.00N	5.0N	7.5N	10.0N
0	0.3080	0.3105	0.3396	0.3450	0.3380	0.3285	0.2906
70	1.1258	1.1646	1.1576	1.1717	1.1474	1.0883	1.0894

Again the changes are significant, but for the purpose of color changes the acid concentration is not a critical factor in defining the range of potentials over which the change takes place.

The Iron Gallate System

It is well known that iron gallate in oxidized form is black and colorless when reduced. Such a reaction, if it can be used electrically, should therefore be useful as an electro-optical shutter.

Early experiments indicated that the iron gallate system alone was not practical since oxidation in the air readily took place and even if this was prevented the previous experiments reported above showed that more precise changes can be effected in a dual system.

The basic system to be tried was,

0.04M Ceric ammonium sulphate
20g/l Ferrous ammonium sulphate
20g/l Gallic acid

in 1N sulphuric acid. The experimental set-up was as before, the ceric ammonium sulphate being the reagent added via the burette. Potentials were measured between a calomel half cell and a bright platinum electrode.

Unexpectedly, this system gave a potentiometric titration curve similar to that for a single reagent system (Figure 29) despite the presence of two redox systems. In dilute acid; i.e., up to 0.3N sulphuric acid, the ferrous gallate became oxidized on standing in the air. The addition of the ceric salt did not bring about marked color changes as expected, and the changes observed were dependent on the acid concentration. Attempts were made to improve the color change by the use of potassium dichromate or ferric ammonium sulphate as oxidants, but with no distinct advantage.

Experiments were then carried out to see whether the system could be used in a cell to produce color changes by changes in potential applied to electrodes inserted in the cell.

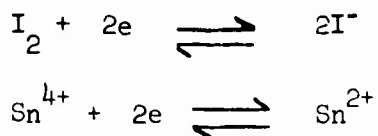
Experiments were then carried out to see whether the system could be used in a cell to produce color changes by changes in potential applied to electrodes inserted in the cell.

It was found that the action produced depended on the acid concentration. When 0.5N or 1.0N acid was used, only a very faint tinge of black was observed on the anode side. When dilute acid was used (less than 0.5N), a black color was formed, but on reversing the applied potential the black color remained. It therefore appears that the black color is a stable oxidation complex which resists reduction at least by electrical methods.

Since other more promising systems were under investigation, it was decided not to pursue any further work with iron gallate systems.

The Tin-Iodine System

This system relies on two basic reactions occurring together:



If into this system is placed an indicator that changes color by reaction with iodine, then the system can be used as a possible source of electro-optical color changes or as an electro-optical shutter. The obvious indicator is starch solution, which changes to a dark blue-black with iodine. but this was found to be unsuitable, because, in the presence of stannous chloride, the color is destroyed and does not re-appear on the addition of excess iodine. Sodium starch glycollate is a suitable indicator over a short period, but after a time coagulation takes place. Probably one of the best indicators found with this system was a suspension of polyvinyl alcohol in ethanol-water, which produces a purple colour with iodine. Polyvinyl alcohol contains acetyl groups, and, if complete de-acetylation is carried out, the colour then produced with iodine is a deep blue. However, if polyvinyl alcohol contains an

appreciable number of acetate groups, then a red color is produced with iodine. Systems containing polyvinyl alcohol as indicator were therefore investigated.

To define the potential range involved in the required color changes, a potentiometric titration curve was produced by titrating 50mls of 0.01N iodine dissolved in 10% potassium iodide with 0.01N stannous chloride solution in 0.1N hydrochloric acid. The results shown in Figure 30 are reversed to those normally given for these type of curves, because here titration is with the reducing agent and not with the oxidizing agent as previously. It is clear that a sharp transition is given, and therefore the system is a possible one for electro-optical effects.

An attempt was made to 'drive' this system electrically, but in this case, the anode and cathode compartments were separate beakers connected by a salt (KCl) solution bridge. In the cathode compartment was also placed a bright platinum electrode and a standard calomel half cell, so that changes brought about in this compartment could be recorded. Nitrogen was bubbled through both compartments, which were closed so that air oxidation could be minimized or eliminated.

The first experiment had in each compartment equal volumes (70ml) of a solution made up of 0.01M iodine in 10% potassium iodide plus 0.1M stannous chloride all in 0.1N hydrochloric acid. With copper electrodes and an applied voltage of 1 volt, the cathode reaction proceeded quite well, but the anode reaction did not. On reversal of the potential, no increase in measured potentials was found as expected in the cathode compartment, but the measured potential continued to fall (see Figure 31).

Since the question of overvoltages at electrodes may be involved, different electrodes were then tried. An experiment with a gold anode and a copper cathode also failed. Raising the voltage to 6 volts only resulted in depositing tin on the copper electrode without any favourable result for the major reaction.

A change in concentrations of the reactants and electrodes produced other effects. With 0.001M stannous chloride in 0.1N hydrochloric acid and 0.001M iodine in 10% potassium iodide also in 0.1N hydrochloric acid and with platinum electrodes the anode reaction proceeded (production of color) but the cathode reaction (colorless) did not. The results shown in Figure 32 were obtained by applying a voltage of 1 volt. Changing the material of the cathode to gold, mercury, carbon or copper failed to improve the reaction.

Driving of Cells

The same technique was used to investigate the application of potentials to other redox systems.

(a) Single $\text{Fe}^{2+}/\text{Fe}^{3+}$ System

Solution: 0.1N ferrous ammonium sulphate
0.1N ferric ammonium sulphate

both in 0.1N sulphuric acid. Mixed in equal volumes, and 7 Omls of the mixed solution placed in each beaker.

No indicator: electrodes of copper.

Applied voltage 1.2V. Results: see Figure (33).

(b) Mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ System

Solution: 0.1N ferrous ammonium sulphate in 0.5N sulphuric acid.

0.1N ceric ammonium sulphate in 0.5N sulphuric acid.

Equal volumes mixed, and 7Omls in each beaker.

Indicator: 1:10 phenanthroline ferrous sulphate.

Applied voltage: 1.2V.

- (i) Copper electrodes Both solutions went red from the intermediate color of purple.
- (ii) Lead electrodes Similar result to (i).
- (iii) Carbon electrodes
Anode: Slow development of blue color.
Cathode: Red developed quickly.
- On reversal of current, the blue color went red quickly, but the red would not reverse.
- (iv) Mercury electrodes similar to (iii).

The measured potentials of experiments (iii) & (iv) are given in Figure 34.

As a result of these experiments, it was thought that the Fe^{2+} ion was too stable in 0.5N acid, so further experiments were carried out with 0.04M ferrous ammonium sulphate and ceric ammonium sulphate in 0.1N sulphuric acid.

- (v) Mercury electrodes Both solutions went slightly blue, and a film formed on the mercury surface.
- (vi) Copper electrodes Both solutions went red.
Figure 35
- (ii) Silver electrodes Both solutions went red, and the electrodes became covered in a film.

- (viii) Lead electrodes Sulphate film tended to build up on the surface of the electrodes.
- (ix) Gold anode, copper cathode This combination worked well, but the solution in contact with the copper cathode appeared to go redder more quickly than the other solution went blue in contact with the gold anode. See Figure 36 for results.
- (x) Gold anode, copper cathode: Variation of Acid Concentration

Consideration of the transition potential of the indicator, 1:10 phenanthroline ferrous sulphate, showed that it could be lowered to lie midway between the electrode potentials $\text{Au}/\text{Au}^{3+} = 1.54\text{V}$ and $\text{Cu}/\text{Cu}^{2+} = 0.337\text{V}$ if the acid used in the reaction was 4.8M. Accordingly, the ferrous and ceric ammonium sulphates were kept at the concentration of 0.04M but made up in 4.8M acid. However, the same effects as those found in (ix) were again observed. Results are shown in Figure 37. From these results, it seems that the reaction works better in dilute acid.

The system, even so, needs more investigation in this form, because eventually both half cells finish up with a red color that cannot be reversed.

Use of Small Cells

At this point, the question of producing changes in cells by application of electrical potentials was analyzed further in the light of the observations already made. One feature that required further investigation was the physical dimensions of the cells, since ultimately very tiny cells should be involved in camouflage. Changes that may require long periods, or even be impossible in large cells because of the diffusion of ions involved may be feasible in smaller cells.

As a first stage in this reduction in size of cells, the effort to measure the potentials produced was abandoned temporarily, and emphasis, put upon producing color changes reversibly in short periods of time. The first smaller cell to be used was 1cm long and 1cm diameter in each compartment separated by a sintered disc (Figure 11). This cell is still gross to the ultimate size envisaged for the final objective, but it did help in establishing useful data.

- (a) The $\text{Sn}^{2+}/\text{Sn}^{4+}$ and $\text{I}^-/2\text{I}^-$ System

Solutions: 0.001M iodine in 10% potassium iodide in 0.01N HCl
0.001M stannous chloride in 0.1N HCl

Mixed in equal volumes & placed in the two halves of the cell.

Electrodes: Carbon.

Indicator: Sodium starch glycollate.

Applied voltage: 0.75V.

Result: Color changed from black to blue but did not proceed further to colorless.

Anode Reaction (Black color):



proceeded quite quickly (15 seconds).

Cathode Reaction (towards colorless)

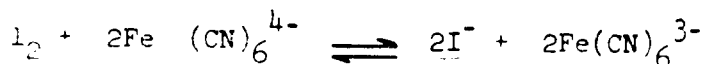


proceeded slowly and incompletely in 20 minutes.

The indicator tended to coagulate.

(b) The $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ and $\text{I}_2/2\text{I}^-$ System

Reaction involved:



Solutions: 0.2M Iodine in 10% potassium iodide in 1N sulphuric acid.

0.2M potassium ferrocyanide in 1N sulphuric acid mixed
in equal volumes and placed in the cell.

Electrodes: carbon.

Indicator: polyvinyl alcohol containing acetate groups color change:
crimson \rightleftharpoons pale yellow.

Applied voltage: 1.4 Volts.

This cell worked well and reversed, in 4 minutes. When polyvinyl alcohol containing acetate groups was used with borax present, a colour change from deep blue to pale yellow was achieved.

(c) $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ System

Solutions: 0.04M ferrous ammonium sulphate in 1N sulphuric acid.

0.04M ceric ammonium sulphate in 1N sulphuric acid.
mixed in equal volumes and placed in the cell.

Electrodes: carbon.

Indicator: 1:10 phenanthroline ferrous sulphate.

Applied voltage: 0.75 volts.

A colour change from red to blue was obtained, which was reversible. Time of reaction, 15 seconds.

(d) The $\text{Ce}^{3+}/\text{Ce}^{4+}$ System

Solutions: 0.04M ceric ammonium sulphate in 0.1N H_2SO_4

0.04M cerous ammonium sulphate in 0.1N H_2SO_4

mixed in equal volumes and placed in the cell.

Electrodes: carbon.

Indicator: Xylene Cyanol FF (Triphenylmethane dye).

Applied voltage: 1.2V.

A color change of green to orange took place quickly, but reversal took 15 minutes.

(e) Universal Indicator

Solution: Universal indicator solution with sodium chloride added.

Electrodes: carbon.

Applied voltage: 2 volt.

A whole range of colors was obtainable, and these were reversible within a time interval of 30 seconds.

The indicator solution would not work unless electrolyte was present and clearly indicated a pH change as the controlling reaction, but this is on strict definition still a redox reaction.

(f) The Potassium Iodide System

Solution: 0.1M potassium iodide in 0.1N H_2SO_4 .

Electrodes: carbon.

Indicator: 1.0% polyvinylalcohol + 5% borax in 0.1N H_2SO_4 .

Applied voltage: 0.75 volts.

The colour change was a dark blue to a light blue, or without borax, crimson to pale pink.

Slow reaction and reversal took 20 minutes.

(g) Dyestuffs

Some unsuccessful experiments were carried out with Dispersol Diazo Black B150 as an indicator for system(e), and with Duranol Blue G, which, being an anthraquinone, should change color on reduction. Some success was achieved with Indigo Carmine in sulphuric acid, which changed from blue to green with an applied voltage of 1 volt.

It is probable that other dyestuffs, especially anthraquinones, will be successful and the conditions for carrying out the reactions electrically need to be investigated. Further work is reported later.

NOTE It should be emphasized that if indicators are to supply the color reaction then the use of dual redox systems seems imperative to get sharp color changes.

The Use of Gels

Reactions up to this point have been carried out in aqueous solution, but at some point, successful systems will need to be applied to textile materials, and aqueous systems as such will be inconvenient. As a first stage towards studying more solid systems, the formation of gels containing suitable salts, etc was studied. Cells containing these gels were then investigated:

1. Polyvinyl Alcohol

The 1.5% polyvinyl Alcohol in water produced a good gel which was slightly yellowish in color. It had the advantage of also acting as an indicator in the iodine/ferrocyanide system.

2. The 5% methyl cellulose, produced a clear very viscous liquid, and 10% produced a white solid gel, so that an intermediate concentration may be useful in cells.

3. Polyvinyl Pyrrolidone

The 5, 10, and 20% polyvinyl pyrrolidone all produced clear liquids, and therefore this substance is not of use, except perhaps in high concentrations.

4. Agar

A 5% solution produced a gel which was yellow-brown in color and too concentrated for the present purpose. A lesser concentration would therefore be useful.

5. Gelatin

A 5% gelatin solution gave a good clear gel.

Gels used in Cells

Concurrent with the research on redox potentials was also work on the use or production of transparent electrodes. This work is reported in another section so that details are not given here, but such transparent electrodes were employed in making suitable small cells in which all the rest of the work was done.

For the work on gels, small cells of the type shown in Figure 38 were used. The spacer was a microscope slide spacer, which is supplied conveniently with a centimetre diameter round hole 1mm deep. The faces of the cell were made of a home-made tin oxide transparent material, and connections to these electrodes was made via aluminium paint, painted on the surface of the tin oxide electrode.

To try out this cell, a gel made of the following and placed in the cell:

1.5% polyvinylalcohol
0.8% iodine
0.8% potassium iodide
Enough potassium ferrocyanide to neutralize the iodine present.
Applied voltage: 3 volts.

On application of the voltage, a dark blue color developed at the anode within 2 minutes, and on reversal of the current, a complete reversal of colors took place. This cycle can be repeated. Due to the unevenness of the coating on the electrode, the color was also uneven, because the color appeared to be deposited on the electrode and not into the bulk of the gel, so that the uneven resistivity of the coating produced uneven deposition of color. The resistance of the electrode varied between 5-200 ohms, and work to improve transparent electrodes is reported elsewhere.

If the applied voltage was greater than 3 volts, gas was evolved, and the cell then ceased to function. This therefore emphasized that the operating voltage for a cell to function must be lower than the voltage required for the liberation of gas at the electrodes. Fortunately, in most cases this condition can be realized.

Chromaticity Co-ordinates of the PVA-Iodine System

The above experiment shows that the use of flat cells formed with transparent electrodes makes electro-optical effects feasible for camouflage purposes, although, of course, much more development is required. The use of iodine with a suitable indicator also makes it possible to use the system as an electro-optical shutter, although as pointed out above, different colored effects can be produced also in this system by the conditions of indicator usage. However, if the conditions are chosen so that a black (or very dark blue) alternates with a colorless solution, then color can be displayed by such a system by including an inert color (say a pigment) in the cell so that, if the black is produced on the electrode, no color will be seen; in the colorless mode of the reactants color will be displayed by the cell. This approach is attractive, because colors can be chosen that are light resistant and of the right shade for the purposes of camouflage.

Of importance in this approach to the problem is the speed of response of the cell; this aspect can be studied by methods already described. The attenuation of the light is also of importance, and this will depend on the concentration of the reagents. As a guide to this aspect of the problem, the chromaticity co-ordinates were determined for a series of solutions of different concentrations held in a cell similar to that described. The actual tristimulus values were measured in transmission with a 'Color-Eye' (Signature Model TM) through a cell containing the reagents, against a blank, a cell containing no solution. In this way, it was hoped to determine the optimum conditions and stability for future experiments with this system:

Solution: (0.5% Polyvinylalcohol
 A((0.5% Borax

 (0.1% Iodine
 B((1.0% Potassium iodide

 All in 0.1M sulphuric acid.

The results are shown in Table 9. All readings were taken 15 minutes after mixing the solutions, since the solutions go darker; i.e., Y(CIE) decreases, with time. Samples 4 and 5 remained in solution several days, whereas the other samples separated out into a colored layer and a clear layer after 24 hours, but this could be avoided by the use of gels.

Of interest was a similar experiment without borax, where a red color instead of a deep blue was obtained.

Solution: A 0.5% Polyvinylalcohol

 B (0.1% Iodine
 (1.0% Potassium iodide

 all in 0.1M sulphuric acid.

The attenuation of the transmitted light was not as good in this experiment as in the former one (see Table 10). It can thus be concluded that suitable electro-optical shutters can be made by the use of borax in this system, but without it the system is probably of more value for the production of color by electro-optical means.

Viologens as Redox Indicators

The use of viologens as redox indicators has long been known, but recently a successful use of N, N¹-di-(n-heptyl)-4, 4¹-bipyridilium dibromide (heptyl-viologen dibromide) has been announced by Philips (BP 1,302,000) for use with

electrochromic display devices. Other similar compounds have also been used for similar usage, and since they are of different colors according to the particular viologen, their use for camouflage is clearly indicated as probable. Their extreme toxic nature must, however, be noted.

Early work was first designed to check the use of the heptyl compound for an electro-optical shutter in the camouflage system, and cells of different design were tried. The solution in all these experiments was:

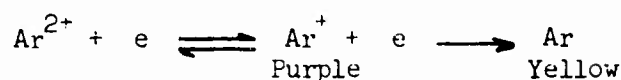
0.1M heptylviologen dibromide plus 0.34 potassium bromide in water.

- (a) A simple cell comprising a small tube filled with the solution into which two gold wires were inserted was first tried. On application of a potential of 1 volt a purple layer was instantaneously formed on the cathode. On switching off the current, the layer on the cathode disappears, probably due to dissolved oxygen in the solution. Voltages lower than 1 volt can operate the system, but the lower limiting voltage has not been determined.
- (b) A cell similar to that described with transparent electrodes was used, except only one electrode was transparent; the lower electrode, however, was a copper sheet. This cell worked well with a purple layer forming on the cathode on application of a potential of 1 volt. Again the layer disappeared on switching off the current, and a thin film appeared on the copper anode after a short time. The system is, however, reversible, so that on reversing the current, the purple layer will disappear from the transparent cathode and form on the copper electrode (which is then the cathode).
- (c) Another cell variant was a 1" length of glass tube 1/4" in diameter. On the inside wall was deposited a thin coating of tin oxide as a transparent electrode. Connection to the inner electrode was made with 'silver' paint. Stoppers through which gold wire was pushed closed the cell, and the wires then became the anode. The same solution filled the cell.

On application of a potential of 1 volt, a purple layer was formed at the ends of the tube. This is probably due to the high resistance of the tin oxide layer. The cell does not reverse well; although the gold wire became quickly coated, the layer on the glass does not clear quickly, again probably due to the relatively large area and the resistance.

- (d) Cell with two transparent electrodes: this is the cell previously described and shown in Figure 8. The solution was again as defined, but before use it was carefully degassed. On application of a potential of 1 volt, a thin purple deposit formed on the cathode and disappeared on reversal. There is a stage in the reversal when both electrodes are clear, so by control of the times involved, this cell can be operated as a shutter.

Application of too high a current produced a yellow color after the purple color on the cathode, with a brownish-yellow color around the anode. The color change at the cathode corresponds to the reaction:



After formation of the yellow color, the cell would not again reverse. The brownish-yellow color at the anode was due to the formation of bromine.

This experiment thus showed that this type of compound is worth further investigation, and that a reversible system is possible if the controlling voltages are not too large.

Similar experiments were also carried out with 'Weedol', a weed-killer that contains small quantities of 1,1'-dimethyl 1-4,4'-bipyridilium ion (paraquat) and 1,1'-2,2'-bipyridilium ion (diquat). This solution is highly toxic and has to be handled with care. A solution containing potassium bromide was prepared and was shown to form a dark colored layer immediately on the cathode, on application of a 2 volt potential, but on switching off the current, the color faded, probably due to dissolved oxygen. Further work with the mixture was not carried out, since other purer compounds with which more precise control could be exercised became available. However, the experiment confirmed the potential value of violognes for the desired electro-optical effects.

Polarography of Violognes

Polarograms with a dropping mercury electrode were taken of solutions of 1,1'-dibenzyl-4,4'-bipyridilium dichloride; i.e., benzyl viologen dichloride 0.001M in potassium chloride (0.1M), and of 1,1'-diheptyl-4,4'-bipyridilium dibromide; i.e., heptyl viologen dibromide (0.001M) in potassium bromide (0.1M).

Results with benzyl viologen dichloride showed steps in the curve of current against voltage of 0.65, 0.9, 1.5, 2.2V, as against reported half potentials are available for this system. Complete results for the heptyl compound are given in Figure 40.

Current-time Curves for Violognes

A cell was constructed of two transparent glass electrodes separated by a glass spacer (1mm thick with a circular aperture 10mm diameter). The cell was filled with a previously degassed solution of 0.1M heptyl viologen dibromide and 0.3M potassium bromide. A linear voltage sweep was applied to the cell, and the current obtained was plotted (Figure 41). A similar cell gave current-time curves at constant voltages 1, 1.5, 2 and 2.5V, Figure 42. These curves are for the production of the reduced species on the cathode and do not include reversal curves.

Table 9

PVA-Borax System

Sample	Solution A	Solution B	Light Trans- mission % Y (CIE)	Chromaticity Co-ordinate	
				x	y
1	1	1	0.88	0.167	0.144
2	1	2	2.74	0.189	0.245
3	1	3	3.21	0.221	0.328
4	1	5	29.67	0.325	0.409
5	1	10	58.98	0.381	0.446
6	2	1	0.96	0.172	0.133
7	3	1	2.75	0.180	0.162
8	5	1	4.21	0.169	0.149

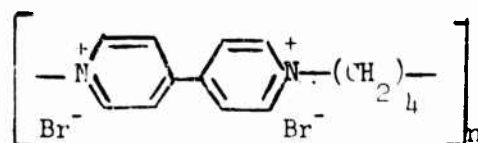
Table 10

PVA alone System

Sample	Solution A	Solution B	Light Trans- mission % Y (CIE)	Chromaticity Co-ordinate	
				x	y
1	1	1	73.63	0.378	0.411
2	1	2	76.65	0.392	0.435
3	1	3	79.13	0.391	0.447
4	1	5	79.93	0.400	0.451
5	1	10	81.43	0.402	0.456
6	2	1	70.36	0.356	0.386
7	3	1	78.28	0.352	0.371
8	5	1	80.08	0.392	0.356

Further work with Viologens

Poly-N,n-butylene-4,4'-bipyridilium dibromide (I)



can be prepared as a solid with redox properties, although in many uses it is better employed as a gel. The preparation is as follows:

A solution of 4,4'-dipyridyl (7.8g) and 1,4-dibromobutane (10.8g) in dry methoxyethanol (350ml) was refluxed and stirred under nitrogen for five hours. The precipitated pale yellow product was filtered off whilst hot, washed with 2-methoxyethanol and then with acetone. It was then dried in a vacuum oven.

An attempt to form a film of (I) was made by compressing it (0.2g) under a pressure of 40,000 p.s.i. for five minutes. A thin pale-yellow transparent film was produced, which unfortunately adhered to the metal dies, and, in consequence, only small pieces could be removed for use. One such piece, when placed between two transparent electrodes and a potential of 1.5V applied, changed color from pale yellow to deep blue. The color reversed slowly, either by leaving the cell exposed to the air, or by a reversal of current. Although in this form the cell was unsatisfactory because of the slowness of reversal, the potential of a solid in a redox system was thus demonstrated, a fact of importance for possible application to textile systems.

In a separate experiment, the polymer was mixed with gelatin (80(I):20 gelatin), ground together in a pestle and mortar and again compressed to a film as before. However, before putting the mixture in the press, a polymer release compound was first sprayed on to the metal surfaces, which later facilitated the removal of the film.

This film also mounted in a cell, and a voltage of 1.5V, applied, when the cathode became a speckled deep blue. The color was reversed by standing in the air or by the application of a reverse current, but the change was very slow. However, the addition of a little water to the system resulted in some speeding up of the changes.

Gels of the compound (I) in water were more successful, and these were used in conjunction with an investigation of all designs and their operation.

Two cell designs, Figure 43, were used, depending on the measurement made. For the measurement of transmitted light the cell was of design shown in Figure 43(a), in which a hole was left in the anode so that the actual operative anode was a ring of metal or metal halide. The dimensions of the glass spacer were: 10mm diameter hole, 1mm thick and approximately 25mm square. The available surface area of the tin oxide transparent cathode was thus 78 sq. mm. For

measurements in reflected light, no hole was left in the metal (or metal halide) coating of the anode.

In operation for transmission, the radical action was initially formed on the cathode opposite the annular anode and then worked inwards towards the center until the cathode was covered. On reversal, the centre of transparent electrode cleared first. The presence of an electrolyte (usually a potassium halide) in the cell did not eliminate this mode of operation. For actual measurements to be made, the scheme shown in Figure 43(b) was set up. With the cell in place, the reading on a galvanometer connected to the selenium cell was to 100 when no radical ion was deposited on the cathode; i.e., complete light transmission, and it read zero when light was completely cut off. On passage of a current through the cell, a deposit formed on the cathode, causing the galvanometer reading to fall, which was then recorded against time. On reversal of current, the reverse process took place.

In the system for reflection, the anode ring of the previous cell was replaced by a plane sheet of metal or metal halide. The cell was filled with the sample which also contained Tioxide R-CR2 (a British Titan product) to enhance the reflectiveness. The cathode was again a transparent tin oxide electrode. The system used is illustrated in Figure 43(c). Light from a 3 watt bulb was focussed on the aperture of the cell, and the galvanometer, set at 100 for complete reflection and zero for reflection from a black surface. On passage of the current, the galvanometer reading was recorded against time.

Experiments were carried out with several variants to the system; these can be classified as follows:

1. The use of two similar electrodes.
2. Variation of the metal anode, keeping the cathode a transparent tin oxide electrode.
3. Silver/silver salt as the anode, again with a transparent tin oxide electrode.
4. The presence of an adjuvant in the system. An adjuvant is a redox compound that is capable of being oxidized at the anode whilst the radical salt is reduced at the cathode.
5. Miscellaneous.

1. Two Similar Electrodes

Two transparent tin oxide electrodes were used in a cell of the design already discussed. A gel consisting of 5% Compound(I) and 5% gelatin was used as the active component.

The results from these experiments are shown in Figure 44, in which the percentage light transmittance against the time of application of the potential are plotted. Apparently an applied voltage of 2.3V is more effective than 2.2V, and voltages below this have very little effect.

2. Variation of the Anode Substance

(a) A cell in which the anode metal was copper, made to the design shown, was used with the active agent as 5% compound(I) and 5% gelatin. In this cell, the anode is thus virtually a ring of copper, and the results obtained with it are given in Figure 45.

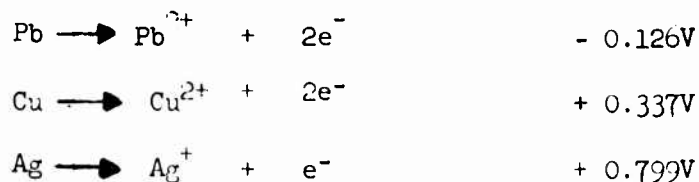
It will be seen from the results in the curve with the operative voltage of 0.5V the speed of operation was about 2 minutes faster than the 0.4V curve, for the formation of the darker compound. However, on reversal, both systems returned to complete light transmittance in about the same total. The return path was found to also occur on shorting the electrodes, but was quicker if a reverse voltage was applied.

The replacement of the tin oxide transparent electrode by the copper anode thus resulted in a reduction in the applied voltage by about 2 volts as well as a quicker reduction in the light transmission.

(b) A similar system to (a) was set up, except for lead replacing copper as the anode. Results are given in Figure 46. It is evident that although the operating voltage was reduced still further, the return to complete light transmission was not achieved.

In addition, the radical cation formed deposits on the lead even whilst standing; i.e., it appears that lead itself reduced the radical salt. Lead is therefore not suitable for an anode material.

A comparison of relevant standard aqueous electrode potentials in acid solution are given below:



(c) A silver electrode in the same system was next used. The cell solution was 5% compound(I), 5% gelatin and 0.33 potassium bromide. Results are shown in Figure 47. Although no coating formed on the silver surface, the cell did not appear to function properly. The reversal of current did not cause the cell to function in reverse for the applied voltage of 0.5V.

3. Silver/Silver salt at the Anode

According to U.S. Patent 3,712,709 (I.C.I.) silver/silver salt anodes are recommended for this type of system. The anode reaction is represented:



On reversal the anode becomes the cathode and the reaction is then:



Thus, i.e., there should be a specific reaction at this electrode.

A number of such electrodes were constructed and used in cells. These include the following:

Silver/Silver bromide
Silver/Silver sulphate
Silver/Silver molybdate

Standard potentials for the anode reactions in acid solution are as follows:



(a) Silver/Silver bromide Anode

The electrode was prepared by electrolysis of 1M potassium bromide solution with a silver anode and a platinum cathode, with a potential of 2 volts for 1 minute. After coating, the electrode was washed with distilled water.

The construction of the cell was as previously discussed. The active solution in the cell was 5% compound(I) and 5% gelatin in water. The results for the percentage reduction in light transmission on operating the cell at different voltages are shown in Figure 48. There was a trend to quicker operating times with an increase in the applied voltage. The results for an applied voltage of 1.3V were different in that the current involved was different from the rest, and almost complete cut-off of light was achieved.

Figure 49 shows the decay curve for an applied voltage of 1.2V, the original light transmission was not quite attained even after 70 minutes of switching off. This effect was due to the ions diffusing away from the electrodes and if the cell was required to maintain complete extinction, then a small applied voltage would have had to be maintained.

A similar experiment was carried out with a solution of 5% compound(I), 5% gelatin in 0.3M potassium bromide as the working medium, and these results are shown in Figure 50. The effect of adding a salt, the anion of which was the same as that of the radical salt, was to lower the required applied voltage. The cell, however, was not completely stable. The results for an applied voltage of 0.4V showed a reversal to almost 100% transmission on switching off the voltage, but this was not found for an applied voltage of 0.5V.

The effect of substituting a silver/silver bromide electrode for a silver one can be seen by comparing all the results just discussed. Thus the silver/silver bromide electrode caused lower percentage light transmissions to be attained for the same applied voltage than with a silver anode, and, at the same time, better reversal characteristics were found.

(b) Silver/Silver sulphate Anode

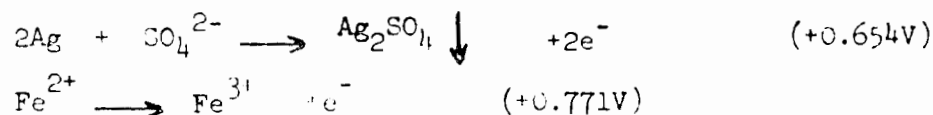
(i) The electrode was prepared by electrolysis of a 1M solution of sulphuric acid with a silver anode and a platinum cathode for 1 minute, with an applied voltage of 2 volts. After preparation, the electrode was thoroughly washed.

The redox cell was constructed as before and filled with 5% compound(I) and 5% gelatin in water. The results are shown in Figure 51. The cell was reversible at an applied voltage of 0.5V but deteriorated at increased applied voltages, as was demonstrated by re-running the cell at 0.5V following use at 0.7 Volts.

A comparison of Figure 51 and Figure 50 shows the effect of replacing the silver/silver bromide electrode with a silver/silver sulphate one. The silver/silver sulphate electrode permitted lower voltages to be used and lower percentage light transmissions were attained. However, there was an apparent voltage limit at 0.6V.

(ii) According to B.P. 1,302,000 (Philips) improvement in these systems can be attained by the addition of adjuvants. An adjuvant in this application is a redox compound capable of oxidation at the anode, whilst the radical salt is reduced at the cathode, on reversal, the oxidized form will be reduced at the same electrode, whilst the radical ion is oxidized at the other. Adjuvants can be either organic or inorganic.

Initially experiments were carried out with ferrous ammonium sulphate as the adjuvant. The cell was filled with 5% Compound(I), 5% gelatin in 0.1M ferrous ammonium sulphate. A silver/silver sulphate anode and a transparent tin oxide cathode was used in the experimental cell. Results for applied voltages 0.7 and 0.9 volts are given on Figure 52. Although on application of the voltage, a good reduction in light transmission was achieved, the cell did not reverse. It was concluded that it was not practical to have both an adjuvant and a silver/silver salt anode because of possible competing anodic reactions. In acid solution the following reactions can occur:



(c) Silver/Silver molybdate Anode

The electrode for this experiment was prepared in a similar way to the above with 1M solution of ammonium molybdate as the electrolyte.

The experimental cell was also similar, but no adjuvant was used. Results are shown in Figure 53 for applied voltages of 0.5 and 0.6V. but the data do not appear to be very promising.

4. The Use of Adjuvants.

Most of the experiments in this section were carried out with the experimental cell constructed for reflection, although one experiment was carried out for transmission. For reflection, titanium dioxide was added to the cell solution to increase the reflectivity, the transmission experiment was conducted without this addition.

Recommended adjuvants from the literature include: 2,3-dichloro-4,5-dicyanohydroquinone, tetrachlorohydroquinone for non-aqueous media and a ferrous salt or a 1,4-di(alkyl-amino) benzene when the solvent was water. Experiments so far, however, have been carried out with hydroquinone as the adjuvant.

(1) Silver Anode, Transparent Tin Oxide Cathode

(a) The working solution for reflection operation was 5% Compound(I), 5% titanium dioxide and 5% gelatin in water. The working voltage was 0.5V, but at this potential, the system was not completely reversible. A test with a cell constructed for transmittance but without the titanium dioxide in the solution also did not reverse, and results were worse for 0.6V than for a 0.5V operating voltage. A comparison of reflected and transmitted light results is shown in Figures 54 and 55. The curve for transmittance appears to indicate a quicker operation at 0.5V than for reflectance; the latter however had titanium dioxide to increase the reflectance.

In the rest of the experiments in this section the cell utilising reflection was used.

(b) Another experiment was carried out with 5% Compound(I), 5% titanium dioxide, and 5% gelatin in 0.01M hydroquinone as the solution in the cell. The results are shown on Figure 56. The percentage light reflected falls quickly, but the return path is much slower.

(c) The concentration of hydroquinone was increased to 0.025M. Results with this system are shown on Figures 57-61. Figure 57 indicates the importance, for comparison purposes, of making sure that the cells are at the same percentage reflectance value before reversing the current. Thus, if the cell is operated too long to give a very low light reflectance, it may become irreversible but can be reversed if the percentage light reflectance achieved in the forward reaction is not as low. This was shown with applied voltages of 0.8V

(Figure 58) where obvious steps are apparent in some of the curves. It was thought that the steps were caused by insufficient hydroquinone being present.

The electrode reactions are as follows:

At the cathode,



At the anode,

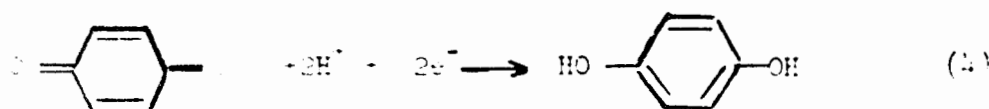


These reactions will continue together until either the hydroquinone or the radical salt is exhausted. If the hydroquinone is exhausted, then reaction (2) will terminate but reaction (1) will continue. On reversal, the reactions occurring are as follows:

At the anode (originally the cathode),



while at the cathode (original anode),



These will continue until all the quinone is converted to hydroquinone. When the current flowing should fall to a lower value, which is observed for the results with 1.6V applied voltage. On the above argument, this suggests that the hydroquinone was exhausted.

Figure 59 is a continuation of Figure 57 and shows the percentage light reflected for voltages of 1.2 to 1.6V; before reversal the percentage light reflected value was kept constant.

An increase in applied voltage results in a shorter operating cycle; e.g., operating cycles vary from 3 minutes (1.0V) to 40 seconds (1.6V). At the voltage of 1.6V, the cell was observed to change to a muddy yellow at the tin oxide electrode followed by the blue colour only when the percentage light reflected was 20%. Steps were observed in the corresponding current curve (Figure 60), but these were expected in the return cycle.

Figure 61 shows the effect of driving the cell back, short circuiting the cell, and open circuiting, for an operating voltage of 1.4V. The return path takes 40 seconds at this voltage compared with 10 seconds for the initial path. Shorting the two terminals results in only 50% reflection in 5 minutes. Switching the current off affects the light reflection very little; e.g., from a value of 12% to only 16%, after a period of 5 minutes.

(d) The composition of the solution in the cell was changed to 2% Compound (I), 5% titanium dioxide, 5% gelatin, 0.1M potassium bromide and 0.01M potassium bromide and 0.01N hydroquinone.

The cell itself consisted of a tin oxide transparent electrode and a silver anode. Results are shown on Figures 62 and 63. The cell operates reversibly for voltages up to 1.0V but not at higher voltages. At the higher voltages, the downward trace in the percentage light reflected curves are characterized by a sudden drop when the current is reversed; this coincides with the irreversibility of the cell. The curve for 0.7V shows a step in the current when the cell reaches 100% reflected.

(e) The concentration of Compound(I) in system (d) was increased to 5%; all other concentrations remained unchanged.

Difficulty was found in keeping the currents recorded within the scale of the microammeter. In previous experiments, the applied voltage was that across the cell, but by the use of the milliammeter it was necessary to calculate the voltage across the cell from a knowledge of the resistance of the recorder and the current flowing.

Results for this system are given in Figures 64 and 65. Again reversing cycles became shorter as the applied voltage was increased, but irreversibility set at an applied voltage of 1.4V. The variation of voltage across the cell is shown in Figures 66 and 67 and the average cell voltages are given in Table 11. These voltages were calculated with the aid of the current curves shown in Figures 68 and 69.

Table 11

Applied Voltage, V_a	Average Cell Voltage, V_c
0.5	0.45
0.6	0.54
0.7	0.62
0.8	0.71
0.9	0.80
1.0	0.91
1.1	0.98
1.2	1.06
1.3	1.13
1.4	1.24

$$V_c = V_a - I.R.$$

(R = resistance of the reversing milliammeter (50 Ω)).

(I = current flowing)

General Observations

All the gels employed in the above experiments were first degassed under vacuum and then purged several times with nitrogen to exclude oxygen.

It was noticed that on application of a potential to cells containing Compound(I), but without potassium bromide being present, the initial colour formed was purple. This rapidly changed to a deep blue as the colour intensified. Cells containing potassium bromide to increase the conductivity, remained purple throughout.

DISPLAY CELLS

The ideas already developed were used in making display cells, to demonstrate how they could be employed for camouflage purposes. These cells were constructed on the shutter principle, the colour being supplied either by coloured paper strips or by pigments actually incorporated in the cells.

1. Figure 70 shows one of the earliest types of display cell. The holes were filled with a gel of 1% agar containing 0.1 M benzyl viologen dichloride and 0.3 M potassium chloride. The top electrode was made the cathode, and on application of a potential, a dark purple coloration was produced, but holes furthest away from the application of the potential were the slowest to form the purple colour, owing to the potential drop across the electrode. The forward reaction is quick, but the reverse is slow in this system. The colour masked or displayed depended on which strip was used in operating the cell.

2. A similar cell was filled with 5% Compound(I), 5% gelatin and with different coloured pigments. Suitable pigments were: Acramin Bordeaux FR, Acramin Yellow F2G, Acramin Blue FFG, Acramin Red FFG, Acramin Green F3G. The top electrode was a tin oxide transparent electrode, but the lower electrode was a silver/silver sulphate anode. The speed of response was quicker than the previous display, but the potential drop along the electrode again was a difficulty.

3. The filling was similar to 2, but in addition 0.01N hydroquinone was included. The bottom electrode here was a silver one. This system is the best so far tried, and the potential drop along the electrode hardly affected the operation.

Other Cell Designs

1. A cell constructed as shown in Figure 71 was filled with 0.1 M heptylviologen dibromide and 0.3 M potassium bromide. On application of 2.5V a purple colour developed on the tin oxide cathode. The colour appeared opposite the small gold anode at first, and then spread to the rest of the of the cathode. The cell proved slow to reverse.

2. A second cell with a silver/silver bromide anode was constructed and filled with 0.1 M heptyl viologen dibromide, and on application of 2.5V a purple colour was rapidly produced. The cell appeared to be reversible.

Other cells and designs are being tested.

Notes on the Use of Adjuvants

It has been already pointed out that beneficial results can be obtained with Compound(I), by the use of various adjuvants. However, there are difficulties that occur by the addition of these reagents to the cell contents.

Potassium ferrocyanide (0.1 M) added to 0.05% of Compound(I), in 0.1 M potassium bromide solution, immediately turned purple owing to the reducing action of the potassium ferrocyanide. Hence potassium ferrocyanide cannot be used as an adjuvant in this system. If 0.1 N potassium ferricyanide was used instead, a yellow precipitate formed, again eliminating potassium ferricyanide as an adjuvant for the system.

Compound(I) in the presence of hydroquinone, benzoquinone, tetrachlorohydroquinone and N N N'N'-tetramethyl p - phenylene diamine dichloride, appeared to be stable, although the latter does tend to cause a purple colour to appear if left in the presence of air. Further tests were therefore carried out.

Benzoquinone

(a) A cell containing 1% Compound(I), 0.1 M potassium bromide and 0.005 M benzoquinone with an applied voltage of 1.0V, gave a colour change, instantly reversed by reversing the current. Reversal also came about without the use of a reverse potential owing to the oxidizing power of the benzoquinone.

(b) A combination of 1% Compound(I), 0.1M potassium bromide and 0.001 M benzoquinone in the cell gave a colour change at 0.9V, which was also quick to reverse. However, below 0.5 V and above 1.5V no colour was produced. An alteration of the concentration of the benzoquinone to 0.0001 M did not change the situation. An increase in the concentration of the Compound(I) to 2.5%, keeping the benzoquinone at 0.0001 M, only resulted in a deeper colour being produced; all other characteristics were the same as before.

Hydroquinone

Using 0.5% Compound(I), 0.1 M potassium bromide and 0.01 M hydroquinone with the applied potential of 0.9V, gave a good colour change which was reversible on reverse current. Increasing the concentration of Compound(I), to 1% and reducing that of hydroquinone to 0.005 M also operated successfully with 1 volt.

Tetrachlorohydroquinone

A combination of 1% Compound(I), 0.1 M potassium bromide and 5 mls of saturated tetrachlorohydroquinone, all made up to 10 mls, operated successfully in a cell at 0.6V, but was somewhat slower than other cells to reverse.

N N N¹ N¹ - Tetramethyl-p-phenylenediamine dihydrochloride

A cell containing 1% Compound(I), 0.1 M potassium bromide and 0.0025 M in this adjuvant gave a colour change at 0.5V, which operated quickly in both directions. If the current was applied for too long and then reversed, a purplish color developed; this was believed to be caused by the oxidation of the adjuvant.

Ferrous Ammonium Sulphate as Adjuvant

The cell used in these experiments had a transparent tin oxide cathode and a silver anode. It contained a gel consisting of 5% Compound(I), 5% titanium dioxide, 5% gelatin and 0.5 M ferrous ammonium sulphate.

Results obtained with this system are illustrated in Figures 72 and 76. For all the curves except where indicated otherwise, reversal was brought about by the application, of a reverse voltage. The results show that the cycle times shortened for an increase of applied voltage. Thus for an applied voltage of 0.6V the cycle time was in excess of 8 minutes, but for applied voltages of 3.0 and 2.6V, the cycle time was in excess of 8 minutes, but for applied voltages of 3.0 and 2.6V, the cycle time dropped to 30-40 seconds. Reversal was also brought about by switching off when a slow recovery took place. (Figure 76).

Figure 77 and 80 show the respective current curves for the above experiments, the sharp maxima in these curves occurring at reversal of the voltage. Figures 81 and 84 show the relation between the applied voltage and the actual voltage across the cell in these experiments.

N N N N¹ - Tetramethyl-p-phenylene diamine dihydrochloride

[Compound (A)] as Adjuvant

Freshly made solutions of Compound (A) mixed with those of Compound(I) resulted in a rapid formation of a deep blue colour due to the reduction of Compound(I). A freshly made solution of (A) in water also turned violet slowly on exposure to air oxidation. Both these reactions could be suppressed by the date given in the Table:

<u>Vol of (A) (0.025 M)</u>	<u>Vol of 0.1 M Na₂SO₃</u>	<u>Colour in 24 hrs.</u>
5 mls	0.5	Violet
5 mls	1.0	Violet
5 mls	2.0	Pale Violet
5 mls	5.0	Colourless
5 mls	10.0	Colourless

A cell was accordingly filled with the following solution: 5% Compound(I), 5% titanium dioxide, 5% gelatin, 0.025 M Compound (A) and 0.01 M sodium sulphate. Very good results were obtained with this system.

Figures 70 and 73 show percentage light reflected values against time for increasing applied voltages. Cycle times became shorter as the applied voltage was increased. (N.B. this cell could not be driven back, but it did return to its original state on shorting the cell terminals.) A fairly constant cycle time of about 50 seconds was attained for applied voltages of 1.6 to 3.0 volts.

Figure 89 shows the percentage light reflected against time when the cell was taken down to a value of 10% light reflected and then switched off. The cathode layer was apparently stable for a number of minutes before it began to fade.

Figures 90 and 91 show the corresponding current curves. These contrast markedly with previous current curves obtained for other systems in that a constant current flowed through the cell. Since the currents flowing were constant, then the actual voltages across the cell were constant. The relationship between the applied voltages and the actual voltages across the cell are also indicated in Figures 90 and 91.

It has been stated earlier that the cell could not be driven back. This is only partly true. If the current was reversed for too long, then the percent light reflected first increased to about 85% and then decreased again due to formation of a violet colouration (presumably the oxidation product of $\text{N N N N}^{\text{I}}$ -tetramethyl-p-phenylenediamine dihydrochloride). This process is shown in the current curve as two steps (Figure 92).

If, however, the current was reversed until the percent reflected light reached 85% and was then switched off, then the cell returned to normal. This is shown in the current curve as a sharp drop in current after the first plateau. (See Figure 93).

Note that in both Figures 92 and 93 the applied voltage was 0.6V, and that in the experiment illustrated in Figure 92, after the current was reversed for too long, the cell did not function again.

It has been noticed that if the concentration of sodium sulphate was increased (concentration not known), then it was possible to drive the cell back as well as short it back.

An attempt was made to make cells with Compound (A) and sodium sulphite that were capable of being reversed electrically as well as by shorting as previously. This was done by increasing the concentration of sodium sulphite. The presence of a greater concentration of sodium sulphite meant that the purple oxidation product of Compound (A) which previously formed on electrically reversing a cell, was rapidly reduced to the colourless reduced state. The result was that the cell then functioned reversibly provided that the current in the reverse direction was not passed for too long.

Supplementary experiments involved cells which were similar to those already described, but with increased concentrations of sodium sulphite. In one case Compound (A) was omitted, and the sodium sulphite itself used as the adjuvant. Cells tested therefore consisted of the following:

(a) A gel which was 5% in Compound (I), 0.025 M in Compound (A) 0.02 M in sodium sulphite, 5% in TiO_2 and 7.5% in gelatin.

(b) A gel which was 5% in Compound (I), 0.025 M in Compound (A) 0.1 M in sodium sulphite, 5% in TiO_2 and 7.5% in gelatin.

(c) A gel which was 5% in Compound (I), 0.02 M in sodium sulphite, 5% in TiO_2 and 7.5% in gelatin.

Light reflected curves for system (a) are presented in Figures 94 and 95.

Corresponding current curves are shown in Figures 96 and 97. Voltages on the graphs are the applied voltages which approximated the true voltages across the cell, since the current flowing was fairly constant initially. A comparison of Figures 94 and 95 with Figures 85 and 88; i.e., for a similar cell which was only 0.01M. in sodium sulphite shows almost identical downward curves. Reversal of the current (Figures 94 and 95) reduced the time for the cell to return to its original state when compared with the shorting technique (Figures 85 to 88). Note that when the current was reversed, the current was passed only until the percentage light reflected value reached about 80%; passage of current longer than this resulted in a tendency for the percent light reflected value to decrease again. In this respect, therefore, this cell was similar to that previously described.

The effect of increasing the sodium sulphite concentration still further; i.e., system (b), is shown in Figures 98 and 99. This resulted in a better system. Again the downward curves are almost identical to those shown in Figures 94 and 95 and in Figures 85 to 88. The increase in sodium sulphite concentration to 0.1 M, however, gave a still quicker reversal curve but again the current had to be switched off in the region of 80% light reflected. If the current was reversed for too long, the light reflected value tended to decrease again, but on switching off the current, the cell returned to normal. This was in contrast to the cell with a lesser amount of sodium sulphite, (0.01M), which did not return to normal or function again.

Current curves for system (b) are shown in Figures 100 and 101.

Note that both cells (a) and (b) would also short back to the original state.

Figure 102 shows the variation of percent light reflected with time after taking cell (b) down to a value of 10% light reflected and then switching off the current. This is a slightly slower curve than that shown in Figure 89 for

the cell with 0.01 M sodium sulphite.

Light reflected curves for cell (c) which only employed sodium sulphite (0.02 M) as the adjuvant are shown in Figures 103 and 104. Again there is little difference in the downward curves from those presented for cells (a). The reverse curves, however, take slightly longer than those for cell (a) and at applied voltages of 2.0 and 2.2 the percent light reflected value did not reverse completely to 100%. Lower operating voltages were apparently suitable, however.

Current curves for cell (c) are shown in Figures 105 and 106.

A successful display cell based on cell (b) and employing Acramin dyes had been built.

Comparison of Heptyl and Benzyl Viologens with (I) in the presence of (A)

Since both the heptyl and benzyl viologen dibromides could potentially be employed in the shutter system as well as (I), a comparison of these with (I) were made. Cells were constructed which were 0.1 M in (X), 0.025 M in N, N, N¹, N¹- tetramethyl-p-phenylene diamine dihydrochloride, 0.01 M in sodium sulphite, 5% in TiO₂, and 10% in gelatin, where X represents either heptyl viologen dibromide or benzyl viologen dibromide. As before a silver anode and a tin oxide transparent cathode were used.

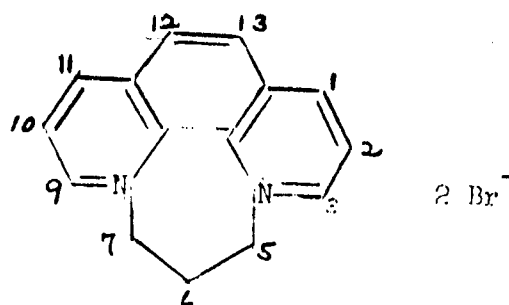
Percentage light reflected measurements for the heptyl viologen system are shown in Figure 107 and seem to be somewhat erratic. Results for the benzyl system are a little better (See Figures 108 and 109). There could be an optimum voltage for this system since both the high and the low applied voltages tried gave slower cycles than more intermediate voltages.

Silver System

It has been found that a solution containing silver nitrate and tetrachlorohydroquinone, with a small amount of sodium nitrite or sulphite (not enough to give a precipitate of the silver salt) will plate silver reversibly on to a transparent electrode. A silver anode was used and a voltage of two volts was applied. Concentrations of silver nitrate, tetrachlorohydroquinone and sodium nitrate or sulphite used were not known since this was only a trial. The plating of silver appeared to be virtually instantaneous.

A solution of silver nitrate and hydroquinone rapidly turned dark but a solution of silver nitrate and tetrachlorohydroquinone only darkened slowly. The latter system was tried, therefore, with a stabilizer present; i.e., as above.

Preparation of 5H-6-7-Dihydro-1,4-diazepino [1.2.3.4.-1 mn] - 1,10-phenanthroline dibromide (II)



(Compound II)

1, 10-phenanthroline hydrate (3g) was refluxed with 1, 3-dibromopropane (2 mls) in 25 mls of acetonitrile for 4 hours. The required solid separated from the boiling liquid as a yellow powder. This was filtered off and recrystallized from absolute ethanol.

The above compound gave a deep red colouration on treatment with zinc dust. It has a reported reduction potential of -0.27 volts.

Initial experiments with Compound (II), were to find a suitable adjuvant to use with it. Compounds tested were hydroquinone, ferrous ammonium sulphate, p-phenylenediamine hydrochloride, tetrachlorohydroquinone, potassium ferrocyanide and a stabilized solution of N, N, N1, N1 -p-phenylenediamine dihydrochloride. Of these the latter two compounds produced red colourations with (II) and were therefore not suitable as adjuvants in this system. The others were apparently suitable since they did not produce red colourations with (II). Of these, hydroquinone was used in cells from which light reflected measurements were made.

Two cells were constructed, which were:

- (a) 0.1 M in (II), 0.1 M in hydroquinone, 2% in TiO_2 and 5% in gelatin.
- (b) 0.1 M in (II) 0.025 M in hydroquinone, 2% in TiO_2 and 5% in gelatin.

A silver anode and a transparent tin oxide cathode were used as before.

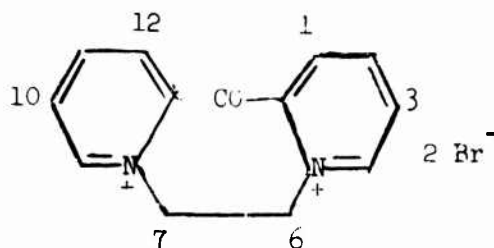
Results for cell (a) are shown in Figures 110 and 111. The percentage light reflected measurements (Figure 110) showed that the cell was not completely reversible at any of the applied voltages tried (0.6V to 2.0V). Corresponding current curves are shown in Figure 111.

As shown in Figures 112 and 113, the results for cell (b), which had a lower concentration of adjuvant (hydroquinone), still demonstrated the irreversibility of the system.

A comparison of Figure 110 and 112 shows the effect of decreasing the concentration of hydroquinone from 0.1 M to 0.025 M. The effect was to give a somewhat slower reaction in the second case.

Colour changes of the cell were orange-red at about 60% light reflected, bright red at about 50% and dark red at about 40%. As indicated by the graphs, the light reflected value never returned to 100%; i.e., the colour never returned to the original yellowish colour. The cell in fact tended to retain the orange-red colour. This apparent light sensitivity might account for the irreversibility of the system.

Preparation of 6,7 - Dihydro - 13 - oxo - 13H - dipyrido[1,2-d:2',1'-g][1,4] - diazepinedi-ium dibromide (Compound (III))



The reported half wave potential of this compound is - 0.11 V independent of pH and concentration. There is no evidence of a second reduction wave. It is stable below pH 5.0. Above this pH value, the salt gradually deteriorates and rapidly breaks down as the solution becomes alkaline. (Black and Summers).

It was prepared as follows:

Di - 2 - pyridyl ketone (6.0 g) was heated under reflux with 1,2-dibromoethane (60 mls) for a total of 24 hours. The solution was cooled, and the dark brown solid obtained was washed with cold acetone and ethanol. It resists recrystallization from acetone-aqueous hydrobromic acid as suggested by Black & Summers.

Use in Cells

(i) A cell containing 5% Compound (III), used for transmission of light with an annular silver electrode, did not work even when the concentration was reduced and voltages up to 3 volts were applied.

(ii) A combination of 0.5% Compound (III), with 0.3 M potassium bromide was used in a cell with two transparent tin oxide electrodes. Application of 1.3 V caused a pale red colour to appear, which could be made to appear more rapidly with 2.0 V. The colour change back to pale brown was successful in reversing the current at both voltages.

(iii) Replacement of one of the transparent tin oxide electrodes by an amalar silver electrode (anode) resulted in a colour change at 0.2 V, but this did not reverse quickly. An increase of the concentration of Compound (III), from 0.5 to 1.0% gave similar results.

(iv) Although other cells were tried with different anodes, the systems all worked at low voltages (0.1 to 0.5 V), but did not reverse easily.

The addition of an oxidant to the system is supposed to quicken the reversing action of the cell, and some experiments to test this were carried out.

(a) A solution of 1% Compound (III). 0.1% potassium ferricyanide, used in the same cell, operated successfully at 0.3 V and reversed quickly. However after several cycles it became slower, and a black coating formed on the silver electrode.

(b) A solution of 1% Compound (III) 0.1% potassium ferricyanide, used in the same cell, operated successfully at 0.3 V and reversed quickly. However, after several cycles it became slower, and a black coating formed on the silver electrode.

(c) A similar experiment, but with 0.1% stannic chloride, gave identical results as in (b).

This problem has been overcome in one instance by "browning" the dark brown colour of the solution by adding a green pigment, (Acramin Green F3G). In this way the compound has been used in 0.25 M concentration (or 5.3%), and the colour change obtained has been therefore from green to brown. (the red colour of the reduced form backed by the green pigment giving a brown colour).

The cell used consisted of a gel which was 3% in agar, 0.25 M in (III). 0.25 M in hydroquinone and with a tin oxide transparent electrode as the cathode and a silver anode. The silver tended to reduce (III) to the red colour. (It is expected that a more inert electrode; e.g., platinum or gold would not do this.) However, the cell still functioned reversibly on applying 1.5 volts, the time for one complete cycle being in the region of 10 seconds.

ANTHRAQUINONES IN REDOX SYSTEMS

Preliminary experiments were carried out with a 0.05 M aqueous solution of the sodium salt of 2;6 anthraquinone disulphonic acid (Compound VI) and various adjuvants (tetrachlorohydroquinone, hydroquinone, ferrous ammonium sulphate and potassium ferrocyanide). Potassium ferrocyanide appeared to be the best in this system, and light reflectance curves were obtained mainly for Compound (IV) and potassium ferrocyanide with different electrodes. It was found that with a metal anode (silver, gold, copper) and a tin oxide transparent cathode a large deposit formed on the metal electrode, but this did not prevent the cell functioning. If two transparent electrodes were used, no dark deposit was formed.

The reduced form of IV was an orange, red colour, whereas the oxidized form was a very pale yellow. Light reflectance measurements were made on the following systems:

(a) A cell comprised of a gel which was 0.05 M in (IV), 5% in TiO_2 , 7.5% in gelatin and with a tin oxide transparent cathode and a copper anode.

(b) A cell comprised of a gel which was 0.025 M in (IV), 0.025 M in potassium ferrocyanide, 5% in TiO_2 , 7.5% in gelatin and with a tin oxide transparent cathode and a copper anode.

(c) A cell comprised of a gel which was 0.05 M in (IV) 5% in TiO_2 , 7.5% in gelatin and with a tin oxide transparent cathode and a silver anode.

(d) A cell comprised of a gel which was 0.05 M in (IV), 0.025 M in potassium ferrocyanide, 5% in TiO_2 , 7.5% in gelatin and with a tin oxide transparent cathode and a silver anode.

(e) A cell comprised of a gel which was 0.025 M in (IV), 0.025 M in potassium ferrocyanide, 5% in TiO_2 , 7.5% in gelatin and with two tin oxide transparent electrodes.

Results for system (a) are shown in Figures 114 and 115. The percent light reflected curves in Figure 1 show the disadvantage of not having an adjuvant present. The percent light reflected fell quite quickly initially, but only rose slowly on reversing the current. The initial light reflected value was not attained after reversing the current for four minutes. Corresponding current curves, are shown in Figure 115.

Results for system (b) are shown in Figures 116 and 117. This system employed potassium ferrocyanide as the adjuvant and was an improvement on system (a). Although the concentration of (IV) was half that used in (a) the percent light reflected fell slightly quicker on applying similar voltages. The return curve on reversing the current was also quicker, but the value of the percent light reflected did not return to 100%. Corresponding current curves are shown in Figure 117.

The replacement of the copper anode in system (a) with a silver anode resulted in a better cell. Results for this system; i.e., system (c), are shown in Figure 118. The light reflected/time curve for an applied voltage of 2.6 volts is shown but this was almost identical with applied voltages between 2.0 and 3.0 volts. This system was completely reversible as indicated in the figure. No current/time curves are available.

The addition of potassium ferrocyanide as adjuvant to system (c) resulted in an improvement. Such a cell; i.e., system (d), gave shorter cycle times. Results for system (d) are shown in Figure 119. The light reflected/time curve for an applied voltage of 2.6 volts is shown with reversal at (i) 15 seconds and

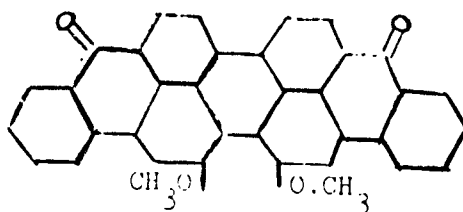
(ii) 30 seconds. The cycle time for (i) was 30 seconds (reversal at 60% light reflected value) and for (ii) was 65 seconds (reversal at 40% light reflected value). As in (c) light reflected/time curves for applied voltages of between 2.0 and 3.0 volts are almost identical with that shown (2.6 volts). Again no current/time curves are available.

Results for system (e), which has (IV) and potassium ferrocyanide in 0.025 concentration, as well as containing TiO_2 and gelatin, with two transparent electrodes are shown in Figures 120 and 123. Light reflected/time curves for applied voltages of 1.5, 2.0, 2.5 and 3.0 volts are shown in Figure 120, and 121 of 1.5, 2.0, 2.5 and 3.0 volts are shown in Figure 120 and 121 indicated current reversal at different values of percent light reflected for an applied voltage of 3.0 volts. Comparison with Figure 119 shows that system (d) was much better than this present system, even though it has earlier been pointed out that the silver developed a dark deposit on it in use. Corresponding current/time curves for system (e) are shown in Figure 122 for the applied voltages used. Figure 123 indicates light reflected/time curves when the cell terminals were shorted and when the current was switched off.

These experiments therefore showed the potential use of anthraquinone derivatives in redox systems. Since a vast range of dyestuffs are derived from anthraquinones, then it is potentially possible to derive reversal color systems by their use.

Experiments with other Dyestuffs

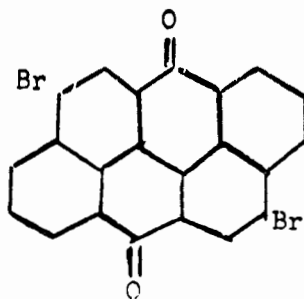
(a) Cibanone Brilliant Green F2B



Theoretical colour change for this compound is from green (oxidized form) to red (reduced form) when in acid solution. The reduced form is dark blue when in alkaline solution.

The above colour changes could be obtained by chemical methods; i.e., reduction with sodium hydrosulphite, but not by electrical means. Attempts were made in (a) aqueous solution (b) alcoholic solution and (c) dimethylformamide, in the presence of adjuvants, to obtain a colour change by application of voltages up to 3 volts. Adjuvants tried were N, N, N^1 , N^1 - tetramethyl -p- phenylenediamine dihydrochloride, potassium ferrocyanide, hydroquinone, tetrachloro-hydroquinone, p-phenylenediamine, ferrous ammonium sulphate and N, N^1 - dimethyl -p- phenylenediamine exalate. Electrodes used were (i) two silver electrodes (ii) two transparent tin oxide electrodes and (iii) one tin oxide transparent electrode and one silver electrode.

(b) Cibacene Brilliant Orange FRK



A similar set of experiments to these described in (a) were carried out but again no colour change was effected by electrical means.

(c) Anthraquinone

(i) In dimethylformamide (100%)

Voltages of up to 3 volts were applied between various electrodes.

With two silver electrodes no colour was produced. The use of two gold or two transparent tin oxide electrodes gave a red colour at the cathode when a voltage of 3 volts was applied. This rapidly disappeared on reversing.

The addition of hydroquinone to the system brought the applied voltage for colour formation down to 2.4 volts.

(ii) In 80% dimethylformamide and 20% methanol

The use of anthraquinone in the above solution with tetramethyl ammonium bromide as supporting electrolyte gave the following results.

With two transparent electrodes a reversible red colour developed at the cathode at an applied voltage of 3 volts. The use of two gold electrodes or one transparent tin oxide electrode (as cathode) and one gold electrode resulted in formation of the red colour at a voltage of 2 volts.

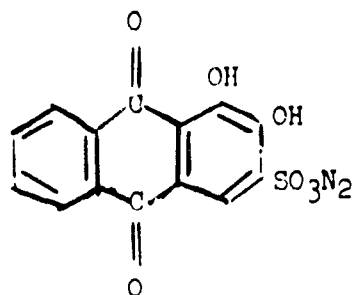
(i) 2-Methyl anthraquinone

In 100% D.M.F. and in the presence of tetramethyl ammonium bromide as supporting electrolyte, a red colour was formed when 2.2 volts was applied between two gold electrodes. The colour change was reversible.

(e) Acramine Yellow F7G

A potential of 2 volts applied between a tin oxide transparent electrode (cathode) and a silver anode resulted in the formation of a dark coloration on the cathode. This coloration partially disappeared on reversing the current. The use of two transparent electrodes and a similar voltage resulted in complete irreversibility of the system: i.e., the dark colour formed but would not disappear.

(f) Alizarin Red S



This compound dissolved in water to give a yellow solution. The application of a potential of 2 volts between two transparent electrodes in the presence of hydroquinone (as adjuvant) and the above compound resulted in formation of a dark colouration on the cathode.. The system was not reversible.

(g) Fluorescein

Fluorescein itself dissolved slightly in water to give an orange-yellow solution. On application of 2 to 3 volts, a dark green colour formed slowly on the cathode (two transparent tin oxide electrodes). The green colour disappeared on reversing the current.

Further work with other dyes will be carried out if required in later stages of the research.

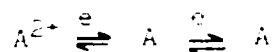
BIPYRIDILIUM REDOX SYSTEMS

It was found convenient in this section to expand the reference to a form of literature survey, because in so doing, valuable information is disclosed that can be used in conjunction with the research work. Reference numbers were not thought necessary since the relevance of the references seemed clear by the description given.

Philips Electrochromic Display Should Prove a Winner.
(New Electronics, 24th July 1973, p. 13)

This article describes a new type of display device developed at Philips Research Laboratories at Eindhoven. The display produced a purple color on application of electric charge. The display offered long-term memory, low switching voltage and good contrast.

The display was based on a redox reaction of diheptylviologendibromide A^{2+} B_{r2} (N,N'-di(-heptyl)-4,4'-bipyridilium dibromide) in water:



The colorless organic compound A^{2+} could be reduced at the cathode in two steps which were determined by other redox potentials. The first step gave a deep blue radical ion $A^{\cdot+}$ while the second gave a slightly brownish product A. The dye $A^{\cdot+}$ gave with the anion Br an insoluble, purple compound $A^{\cdot+}Br$ which adhered to the cathode surface. This colored layer could be erased by reversal of the current.

The absorption band of the colored diheptylviologendibromide A^+ ion was rather broad with a maximum in the green part of the spectrum. The absorption coefficient (α) of the dye was high (α is about $26,000 \text{ cm}^{-1}$).

The article also deals with electrode materials (metallic, high-conductive tin oxide and indium oxide) and with writing voltages and times.

Electrochemical Color Low-Voltage Indicators

(V. V. Treier & B. I. Shapiro - Instrumentation & Control No. 8.

August 1970, p. 66-6)

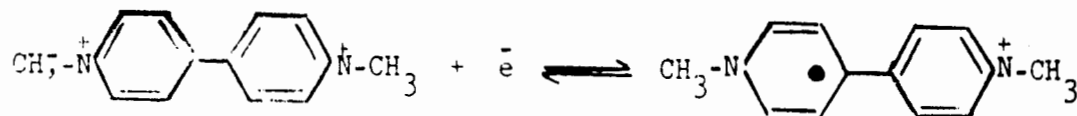
(Original reference - Prib. Sist. Upr. 1970, (8), p.44-45 (Russ)).

Electrochemical color indicators based on eg salts of 1,1'-dimethyl-4,4'-bipyridines with inorganic anions had a high degree of reversibility and would undergo several thousands of reversals.

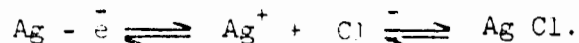
There were 3 cell variants; (1) a 2-electrode indicator without diffusion diaphragm, (2) a 2-electrode indicator with diffusion diaphragm, and (3) a 3-electrode cell with screening electrode.

E.g., with an electrolyte consisting of an aqueous solution of $5 \times 10^{-2} \text{ M}$ 1,1'-dimethyl-4,4'-bipyridine dichloride and M.KCL was used. At a threshold of 0.2-0.3V the indicator began to operate and at 1.0V, the indicator broke down. If the coloured state had to be maintained, a diffusion diaphragm or a screen electrode was used.

Reaction on the cathode:



and on the anode with an Ag/AgCl electrode:



U. S. Patent 3,712,709

A N-substituted p-cyanophenyl derivative of, for example, a bipyridyl was reversibly transformed between the cationic form (colorless or pale yellow) and radical (usually green) by application of a potential between a transparent conducting electrode and a counter electrode.

The active material was comprised of an N(p-cyanophenyl) substituted derivative of a bicyclic compound having two nitrogen containing rings.

The working electrode was comprised of a coating of a conducting oxide or a very thin metal film.

Examples of active compounds were simple salts or polymeric forms of mono- or di-Ni-substituted-p-cyanophenyl derivatives of bipyridyls, diazapyrene, or biquinolyls. The preferred compound is N,N'-di(p-cyanophenyl) 4,4'-bipyridinium dichloride. This formed an insoluble colored radical on the working electrode surface which did not diffuse away and was easily reoxidized to the colorless form by reversal of the applied potential.

The active material could contain the (p-cyanophenyl) group attached to polymeric structure, e.g., a 4-(4'-pyridyl) N-p-cyanophenyl pyridinium salt reacted with polyvinyl chloroacetate or copolymers thereof with polyvinyl alcohol to form an active material. If polyvinyl alcohol units were present these could be cross-linked; e.g., with glycol, to give a gelled active material.

The active material was usually used in the presence of an aqueous medium; e.g., water or a water soluble polymer such as agar, gelatine, methyl cellulose, polyvinyl alcohol or polyvinyl-pyrrolidone. An inert electrolyte could be added to increase conductivity; alkali metal salts such as halides or fluoroborates preferred.

E.g.'s, of anions which could be associated with active materials were halides, especially chloride, SO_4^{2-} , HSO_4^- (where R = an alkyl group), SiF_6^{2-} or BF_4^- .

Several possibilities were available for the counter electrode; it was desirable to precoat the metal counter electrode with radical salt before assembly; this avoided the possibility of gas formation during the first operational cycle. Alternatively, the counter electrode was a metal in contact with an insoluble salt, the anion of the insoluble salt being common to the active species; e.g., Ag/AgCl.

Electrochemical oxidation of the colored species was facilitated by the addition of an easily oxidizable material which was colorless or only lightly colored; e.g., sodium ferrocyanide in 0.1M concentration.

A third electrode could be included as a reference electrode for potential control purposes.

Example

Active material: a layer of an agar jelly stabilized aqueous solution of N, N'-di(p-cyanophenyl) 4,4'-bipyridinium dichloride. The concentration of active component was 10^{-3}M in 0.1N aqueous sulphuric acid.

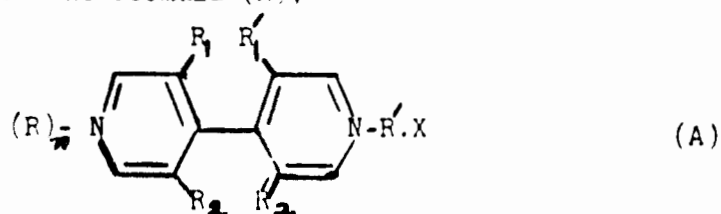
Voltages used: -2.2V relative to Ag/AgCl reference electrode applied caused deposition of the insoluble green radical cation. Application of -0.4V caused the undesirable 2 electron reduction. The green color was stable for several hours on open circuiting. Reversal of the potential to +1.0 volts caused bleaching in one minute.

The use of an active composition made from $10^{-3}M$ N, N'-di(p-cyanophenyl), 4,4'-bipyridinium dichloride, 0.1M KCl and 0.1M $Na_4Fe(CN)_6$, gelled with 5% gelatin gave a device which could be bleached rapidly with an applied potential of +0.4V (relative to Ag/AgCl chloride reference electrode).

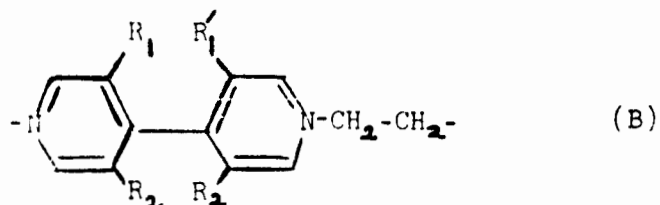
Good results were also obtained by replacing the active compound with a copolymer of polyvinyl alcohol and polyvinylchloroacetate, the latter groups being quaternised with 4-(4-pyridyl)-pyridinium chloride. The copolymer could be cross-linked by immersion in glyoxal solution.

Patent Specification 1,302,000 (Jan 1973 - Philips Electronic & Associated Industries Ltd.)

This covers compounds of the formula (A),



where R & R¹ each represented an alkyl or cycloalkyl group containing up to 12 carbon atoms or an unsaturated alkyl or cycloalkyl group containing up to 12 carbon atoms or an aralkyl or alkaryl group containing up to 10 carbon atoms or a phenyl group, which groups could be substituted in the aromatic nucleus with CF₃, a halogen, CH₃, OCH₃, or NO₂, a carbonamido-alkyl group in which the N atom could carry one or two alkyl groups which together with a hetero-atom may form a ring, which group or groups could contain up to 16 carbon atoms, an alkoxy-carbonyl-alkyl group containing up to 16 carbon atoms, a thienyl alkyl group containing up to 10 atoms or a nitrile group, whilst R could also be the group of formula (B),



In which formulae R₁ & R₁ each represented a H atom or together a -CH=OH- group; R₂ & R₂ each represented a H atom or together a -CH=Ch group; n was zero or unity and X represented an electrochemically inert anion.

Examples of R & R¹ was methyl, n-propyl, iso-propyl, sec-butyl, n-heptyl, allyl, benzyl, 3,5-dimethylmorpholinyl-carbonylmethyl, 1-propionylethyl-1, carbon amidomethyl, dodecyl, w-methoxycarbonyldecyl, hexadecanyl, phenyl and 2, 4, 4-trinitrophenyl.

Compounds of the formula (A) in which R represented the group (B) could be prepared from a compound of the formula (A), where $n = 0$, and 1, 2 - dibromo - ethane.

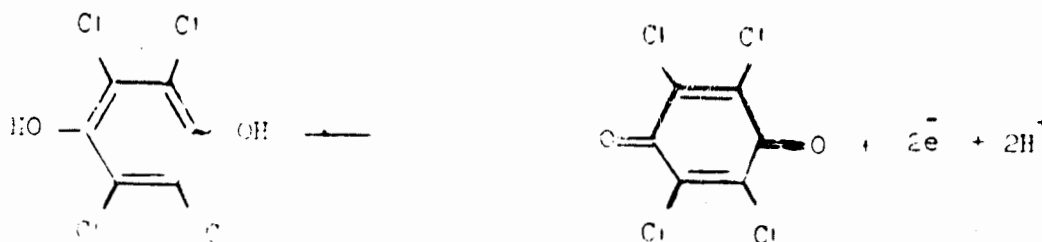
Examples of electrochemically inert anions was perchlorate, boron tetrafluoride, halides, phosphate, etc.

At the cathode $Ar^{2+} \rightarrow Ar^+$

At the anode the adjuvant was oxidized. Suitable adjuvants were substituted hydroquinones which have a redox potential of at least 0.7V (relative to S.H.E.). They included hydroquinones substituted with a halogen, CN, CF_3 , CCl_3 or SCF_3 . Tetra - substituted hydroquinones were preferred; e.g., 2,3 - dichloro - 4,5-dicyanohydroquinone and especially tetrahalohydroquinone, in particular tetrachlorohydroquinone.

Alternatively, adjuvants would be Fe(II) salts. However, anions of these salts had to be inert at the voltages used and in the solvent used. A minimum solubility of about 0.01 mole/l. egs ferrous boron tetrafluoride, ferrous acetate, ferrous chloride etc., was required.

Other adjuvants were 1,4 -di(dialkylamino) benzenes. The alkyl groups present preferably contained 1 to 5 C atoms., as for example at the anode, tetrachlorohydroquinone:



Oxidizable and reducible substances had to be at least 0.01M in concentration with no upper limit to the concentration.

Use of titanium dioxide was suggested as a white background.

Examples of solvents were water and aprotic solvents such as acetonitrile, propionitrile, gentarodinitrile, benzonitrile, propylent carbonate, nitromethane and acetic acid anhydride.

Preferably, the solvent was water when the reducible substances of formula (A) were halides. BF_4^- anions could be used in water. When water was used as the solvent, a Fe (II) salt or a 1,4 -di(dialkylamino) benzene was used as the adjuvant. This was also the case with acetic acid anhydride as solvent.

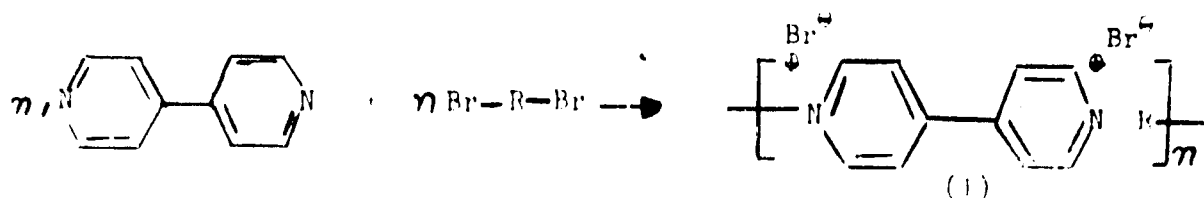
Hydroquinones were preferably used in an organic medium. (N.B.; it has been found that quinolates could give rise to insoluble salts with compounds of formula (A). This was prevented by the addition of a small amount of an acid, either organic or inorganic, (0.5 to 10% by weight.)).

Electrodes could be inert electrodes; e.g., SnO_2 , InO_2 , Pt, Ir and Au. It was not necessary for all electrodes to be made of the same material.

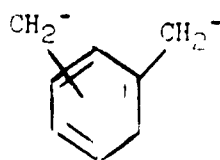
Absence of oxygen was required. Operating voltages were found to be 1.2 to 1.3 volts.

Polyviologens - A Novel Class of Cationic Polyelectrolyte Redox Polymer
(Polymer Letters, Vol. 9, pp 289-295 (1971) by A. Factor & G. E. Heinsch)

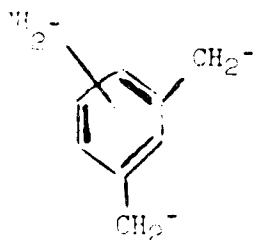
This discusses the preparation of a novel class of polyelectrolyte redox polymers, polyviologens (I) which combine hydrophilic behaviour with a simple one step synthetic route; e.g., (1),



where R = o, m, or p



; $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$; or



These polyviologens belong to a class of ionic polymers named ionenes, formed by the condensation of simple diamines and dihalides. Ionene polymer salts of 7,7,8,8-tetracyanoquinodimethane radical ion (TCHQ^\ominus) containing neutral TCNQ have been found to be highly conductive, with conductivities (25°) of up to $10^{-2} \Omega^{-1} \text{ cm}^{-1}$.

Syntheses of polyxylylviologen dibromides (PXV-Br_2), polyxylylviologen poly(styrenesulphonate) (PXV-(PSS)_2), polyxylylviologen-polyacrylate (PXV-PA_2), polybutenylviologen dibromide (PBV-Br_2), crosslinked polyomesitylviologen bromide (PMV-Br_2) are discussed.

Conductivity of polyxylylviologen TCNQ^\ominus salts are discussed. It was possible to cast films of these materials.

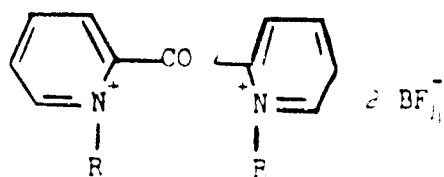
All forms exhibited redox activity.

Electrochemical properties of these materials are considered in a forthcoming publication.

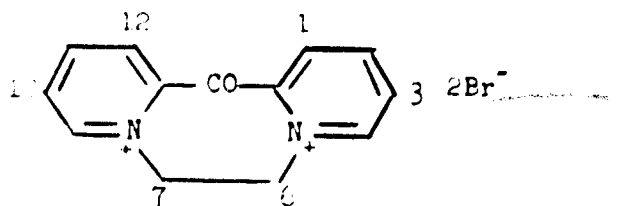
Radical Cations from Diquaternary Salts of Di-2-pyridyl Ketone

(Black, A. L. & Sumner, L.A., J. Chem-Soc (C), 1970, p. 2394)

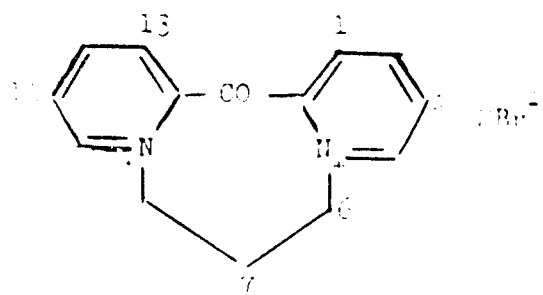
The investigators prepared a number of diquaternary salts of di-2-pyridyl ketone:



(I)



(II)



(III)

(II) = 6,7-Dihydro-13-oxo-13H-dipyrido
[1,2-a:2',1'-b][1,4]
diazepinedi-ium dibromide.

(III) = 7,8-Dihydro-14-oxo-14H-dipyrido
[1,2-a:2',1'-b][1,5]
diazocinedi-ium dibromide.

All were soluble in water. Compounds (I; R = Me) & (I; R = Et) were stable below pH ca. 5.5, and compounds (II) and (III), below pH 5.0. Just above these pH values the salts gradually deteriorated and rapidly broke down in alkaline solution.

The one-electron reduction salts of (I; R = Me) and (I; R = Et) were blue. The corresponding salts of (II) and (III) were deep red and violet.

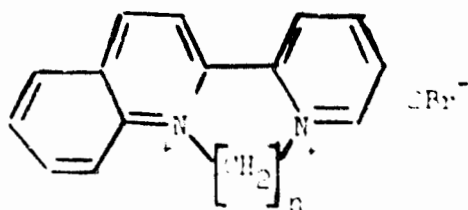
The radical cations were not appreciably oxidized back to the diquaternary salts by air.

The above compounds gave one-electron reduction waves with half-wave potentials against a standard calomel electrode of -0.30V (I; R = Me), -0.32V (I; R = Et), -0.11V(II) and -0.17V(III). There was no evidence of a second reduction wave.

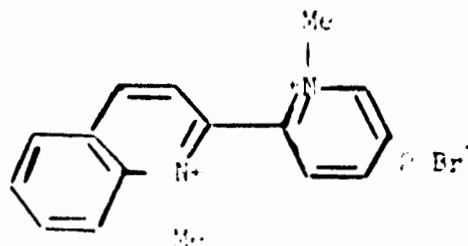
The above salts were tested as herbicides on six plants. The salts (I; R = Me) and (I; R = Et) were inactive at 5 kg/hm² while (III) killed only sugar, but at this application rate. The salt (II) was the most active.

One-electron Transfer Properties of Diquaternary Salts of 2-(2-Pyridyl)-quinoline
(Black, A. L. and Summers, L.A., J. Chem. Soc. (C), 1971, p. 2271)

Prepared a number of diquaternary salts of 2-(2-Pyridyl)-quinoline:



(I)



(II)

I (n=2) = 6,7-dihydropyridine
[1⁺,2⁺:3,4] pyrazine [1,2-a]
quinoline:1,1-bis Dibromide.

I (n=3) = 6,7-dihydropyridine
[1⁺,2⁺:3,4] triazine [1,2-a]
quinoline:1,1-bis Dibromide.

II = N,N¹-dimethyl-2-(2-pyridyl)-
quinoline dibromide.

[of structure of III - liquid]

All the salts were soluble in water and were stable in aqueous solution at low about pH 7, but were decomposed by stronger alkali. Radical-cations produced were coloured red-orange (II), olive green (I; n = 2), and brownish green (I; n = 3). The radical-cations from I (n = 2 and 3) were stable in aqueous solution.

The reduction potentials against a normal hydrogen electrode are given in the Table below together with λ_{max} of the U.V. absorption spectra. 2,2'-bipyridyl salts are given as a comparison.

<u>Pyridylquinoline salt</u>	<u>E₀(V)</u>	<u>λ_{max}</u>
(I; n = 2)	-0.18	356
(I; n = 3)	-0.21	338
(II)	-0.29	327

Bipyridyl salt

(III; n = 2)

(III; n = 3)

 $E_0(V)$

-0.35

-0.55

 λ mμ.

311

257

The salts (I; n = 2 & 3) also gave second reduction waves at about -0.60 to -0.70V, but this was pH dependent.

The salts (I; n = 2 & 3) were reversible one-electron transfer systems. The salt (II) could not be regarded as the oxidized form of a reversible redox system.

In herbicidal tests on six plant species the salts (I; n = 2 & 3) and (II) were completely inactive, while (III; n = 2) was only ca. $1/50$ th as active as Diquat.

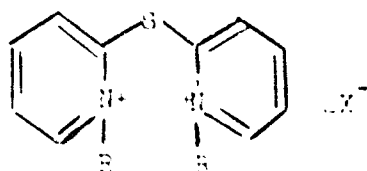
The salt (I; n = 2) possessed unusual fungitoxic properties.

Effect of Introducing a Sulphur Bridge on the Herbicidal Activity of Diquat.

(Summers, L. A., Nature, Vol. 214, April 22, 1967, p. 381)

The author investigated diquaternary salts of 2,2'-dipyridyl sulphide:

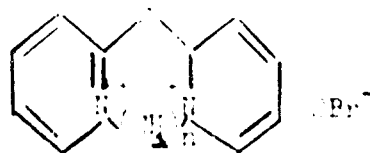
(I)



(I; R=CH₃, X=I) = The N,N'-dimethiodide or 2,2'-dipyridyl sulphide.

(I; R=C₂H₅, X=Br) = the N,N'-diethyl dibromide or 2,2'-dipyridyl sulphide.

(II)



(II; n = 1) = 6H-dipyridyl 2,1-1:1',2'-bis-1,3,5-thiadiazinium dibromide.

(III)



(II; n = 2) = 6,7-dihydrodipyridyl [2,1-b:1',2'-f]-1,3,6-thiadiazepinium dibromide.

(III) = Diquat dibromide.

The diquaternary salts of 2,2'-dipyridyl sulphide gave coloured (usually yellow-green) solutions in water when reduced.

Reduction waves were obtained in solutions of various pHs as tabulated below:

Compound	E_2^1 (pH 5.9)	E_2^1 (pH 6.8)	E_2^1 (pH 8.04)
(III)	-0.61	-0.61	-0.61
	-0.78	-1.00	-1.03
(I; R=CH ₃ ; X=I)	-0.67	-0.67	-0.67
(I; R=C ₆ H ₅ ; X=Br)	-	-0.67	-
(II; n = 1)	-0.74	-0.75	-0.74
(II; n = 2)	-0.63	-0.63	-0.62

E_2^1 obtained versus the standard calomel electrode.

A second reduction wave for diquat dibromide (III) obtained at -1.0V.

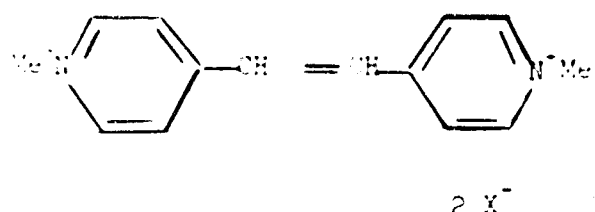
In herbicidal tests the diquaternary salts of 2,2'-dipyridyl sulphide showed no significant activity.

Chemical Constitution and Activity of Bipyridylium Herbicides.

Part V. Diquaternary Salts of trans-1,2-Di-(4-pyridyl) ethylene.

(Dickenson, J. E. & Summers L. A., J. Chem. Soc. (C), 1969, p. 1643)

The author prepared salts of trans-1,2-di-(4-pyridyl) ethylene:



I. X = I

II. X = MeSO₄

Action of zinc powder gave a brownish green solution. If excess zinc was present the solution became pale yellow.

This suggests that the one-electron reduction product was unstable.

Above about pH 7, the compounds above gave a one-electron reduction wave (constant pH and concentration, with a E_2^1 of -0.75V (against a standard calomel electrode). A second reduction wave also occurred with a E_2^1 of -0.91V.

Below pH 7 the half-wave potential of the second reduction wave gradually increased until at about pH7 the two waves merged to give a two-electron wave.

In herbicidal tests, the salt (II; i.e., $X = \text{MeSO}_4$) was slightly active on sugar beet, but was inactive against five other plant species.

The result was consistent with the theory that for high herbicidal activity of the type associated with bipyridilium salts, the compounds must be capable of being reduced at appropriate potentials to radical cations which are stable in aqueous solution, and which are quantitatively oxidized back to the diquaternary salts by air.

Phytotoxicity Control exerted by Redox Potential Values of the Bipyridilium Quaternaries. By B. G. White (Proc. 10th Br. Weed Control Conf. 1970, p. 997)

Bipyridilium diquaternary salts must be capable of being reduced to their radical ions in order to be phytotoxic. The energy required for reduction was measured polarographically, and the site of photosynthetic reduction and efficiency of electron transfer, investigated in vitro. Activity was found to be controlled by redox potential (E_2^1), and allowed the compounds to be separated into three groups:

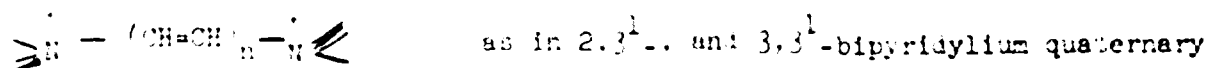
(a) E_2^1 more negative than -450 mV. Activity decreased as E_2^1 increased. Photosynthetic energy was insufficient to allow quantitative radical formation.

(b) E_2^1 more positive than -250 mV. Little or no activity.

(c) E_2^1 -300 to -450 mV. High activity.

Since E_2^1 values correlated with the electronic influence of the quaternary substituents measured by the polar inductive value for the particular group, compounds with the desired redox potentials could be designed.

Analysis of configurations associated with herbicidal activity showed that the main structure $\text{>N}^+ = (\text{CH}=\text{CH})_n = \text{N}^+ <$ as in 2,2,2,4¹ and 4,4¹-bipyridyl derivatives was an essential requirement. The arrangements:



derivatives resulted in inactivity, poorer delocalisation and less stable radicals.

The Relationship Between Herbicidal Activity and Electrochemical Properties' of Quaternary Dipyridilium Salts.

(J. Volke - Collection Czechoslov. Chem. Commun. Vol. 33, (1968) p. 3044-3046.)

Quaternary salts of substituted 2,2'- and 4,4'-bipyridines have proved effective as potent herbicides. The actual condition of herbicidal activity and the ability of the molecule to form a free radical after the reversible uptake of a single electron; the resulting radical was mostly intensely colored.

Other similar compounds to paraquat (1,1'-Dimethyl-4,4'-bipyridilium difluoride) which exhibited similar activity were 1,1'-bis(carbomethoxy)-4,4'-bipyridilium difluoride, 1,1'-bis(hydroxyethyl)-4,4'-bipyridilium difluoride, 1,1'-bis(ethoxyethyl)-4,4'-bipyridilium difluoride.

The fundamental prerequisites of the herbicidal activity on substances of this type was the reversibility in the formation of the radical in the electrochemical sense; i.e., the ability of the radical to be rapidly reoxidized back to the starting compound.

Another powerful herbicide, diquat: -1,1'-ethylene-2,2'-bipyridilium difluoride, gave the reversible formation of a green radical.

The pyrazole ability increased in the quaternary salt of 2,2'-bipyridine, 1,1'-trimethylene-2,2'-bipyridilium difluoride and 1,1'-tetramethylene-2,2'-bipyridilium difluoride, where the steric hindrance caused by the relatively long methylene groups prevented the coplanarity of both pyridine rings. This led to the irreversibility of the reduction and shifted the halfwave potential of the one-electron wave of such a compound to more negative values (see Table 1).

Table 1

Half-wave potential, E_1 , of quaternary salts of 4,4' and 2,2'-Bipyridine, 0.1 M. solution, aqueous borate buffer pH 8.3

<u>Compound</u>	<u>E_1 (S.C.E) V.</u>
1,1'-Dimethyl-4,4'-bipyridilium difluoride	-0.60
1,1'-Ethylene-2,2'-bipyridilium difluoride	-0.61
1,1'-Trimethylene-2,2'-bipyridilium difluoride	-0.72
1,1'-Tetramethylene-2,2'-bipyridilium difluoride	-0.78

If the number of methylene groups in the chain between the two nuclei was increased too far, the coplanarity of the rings was rendered impossible; in contrast to both preceding compounds the reduction proceeded irreversibly.

Note An evidently reversible formation of the colored radical capable of re-oxidation was not sufficient for attaining phyto-toxicity (e.g., the inactivity of benzyl viologen (i.e., the salt of the 1,1'-dibenzyl-4,4'-bipyridilium cation)). Have strong adsorption of the colored radical with benzyl viologen (on Hg).

Comparison of benzyl viologen with morphamquat ((3,5-dimethylmorpholino-carbonyl methyl)-4,4'-bipyridilium dichloride) which was active gave results shown in Table 2.

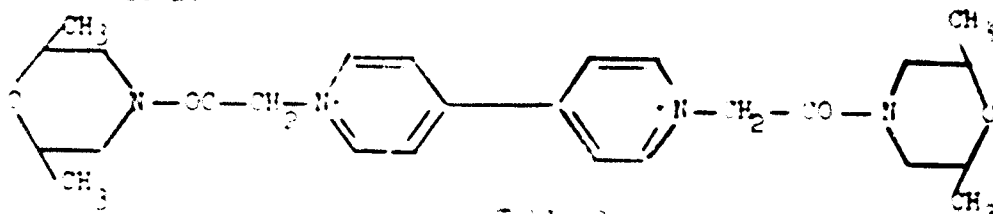


Table 2

Half-Wave Potentials of the Reduction Waves of Morphamquat & Benzyl Viologen
Viologen for Different Depolarizer Concentrations

Phosphate Buffer pH 6.0; half-wave potentials vs. S.C.E. $E_{0.1}$ was the potential at which the discontinuous absorption prewave appeared.

Substance	Conc. $10^{-3} M$	$E_{0.1}$ V	$(E_{0.1})^2$ V	$(E_{0.1})^2$ V	$(E_{0.1})^2 - (E_{0.1})^2$ eV
Morphamquat	0.1	-1.26	-1.54	-1.54	0
	0.2	-1.27	-1.61	-1.61	0
	0.3	-1.28	-1.64	-1.64	0
Benzyl Viologen	0.1	-1.34	-1.80	-1.80	0
	0.2	-1.35	-1.82	-1.82	0
	0.3	-1.36	-1.85	-1.85	0

The potential $E_{0.1}$ (at which a discontinuous absorption prewave appeared) of the 1st reduction wave of morphamquat was more positive than that of benzyl viologen (BV). However, the reverse relationship existed with the 2nd reduction wave.

The radical of BV existed over a much narrower range (2 - 100-220 mV) than in the case of morphamquat (200 - 400 mV). The 1st reduction of the BV radical pre-ceeded at a more positive potential. As a result of this, the pre-oxidation of BV was greater than the active primary radical would be further reduced and then finally eliminated from the electrochemical process.

A greater E value meant a higher stability of the corresponding free radical.

TRANSPARENT ELECTRODES

[illegible]

- 40 -

Preparation of Transparent Electrically Conductive Electrodes

Attempts have been made to produce transparent electrically conducting coatings on glass which have lower resistance per square than the commercially available Baltrason coated glass. Van Boort and Groth (H. J. J. Van Boort and R. Groth, Philips Technical Review, Vol. 39, No. 1, 17-18 (1965)) have shown that tin doped indium oxide films can be produced with resistance per square of the order of 7 to 8Ω for a film thickness of $0.32 \mu\text{m}$. This compares with 170Ω for undoped indium oxide films and 30Ω for heavily doped tin oxide films of similar thicknesses. For a given film thickness Van Boort and Groth report that the curve of resistance per square as a function of tin oxide doping level, for indium oxide films, exhibits a flat minimum between 2 and 3 atomic percent of tin.

Tin doped indium oxide films were deposited as follows on soda glass microscope slides. A solution of InCl_3 in butyl acetate was made up containing approximately 2 to 3 atomic percent of tin in the form of InCl_2 . The exact hygroscopic and weightings were made in the laboratory under ambient conditions; i.e., 20°C and 65% r.h.. This solution was sprayed from an atomizer, onto the hot surface of the glass ($\sim 400^\circ\text{C}$). At this temperature the InCl_3 is converted to In_2O_3 which forms a thin layer on the glass. The thickness of the deposited layers was not known but layers could be produced with the same thickness by observing the color of the layer in reflected light. The coloration in the film is produced by the interference between the light reflected from its upper and lower surfaces and changes in color with increasing thickness, straw-yellow, reddish-yellow, olive green. This sequence of colors then repeats as the thickness of the layer is further increased.

The film on glass with resistance per square of the order of 1Ω was removed and the spraying continued until the films appeared green. The electrodes were then tested and found to have with these electrodes a resistance per square of the order of 1Ω .

APPENDIX 2

TESTING OF CELLS

A number of cells have been tested by a continuous cycling technique at the appropriate voltage. Cells tested were as follows:

(a) This cell consisted of a gel which was 5% in poly-N,n-butylene-4,4-bipyridilium dibromide, 0.1M in hydroquinone, 3% in agar and contained the red pigment Acramin Red FFG. The electrodes were a tin oxide transparent cathode and a silver anode, and the cell was cycled on 1.5 volts.

The cell was cycled 1500 times, the forward forming current being applied for 3 seconds and the reverse clearing current for 4 seconds. At this stage the cell cleared only in parts. Upon resting the cell for 24 hours the cell recovered, and a further 500 cycles were carried out, but further cycling required longer application of the forward and reverse currents. A further 500 cycles were carried out with the forward and reverse currents being applied for 6 and 10 seconds, respectively.

The cell still functioned one month after testing.

(b) This cell consisted of a gel which was 0.25M in 6,7-dihydro-13-oxo-1,4-dipyrido 1,2-d:2',1'-g 1,4-diazepinedi-ium dibromide, 0.25M in hydroquinone, 3% in agar and contained the green pigment Acramin Green F3G. The electrodes were a tin oxide transparent cathode and a gold anode. The cell was cycled on 1.5 volts.

The cell was cycled initially for 500 times, the forward current being applied for 1 second and the reverse current for 1.5 seconds. The cell was then rested for 24 hours before a further 500 cycles were carried out. At this stage the cell remained brown and would not clear at all.

(c) This cell consisted of a gel which was 0.05M in the sodium salt of anthraquinone-2:6-disulphonic acid, 0.05M in potassium ferrocyanide, 2% in titanium dioxide and 3% in agar. Two transparent tin oxide electrodes were employed, and the cell was cycled on 3.0 volts.

The cell consisted of a gel which was 5% in poly-N,n-butylene-4,4'-bipyridilium dibromide, 0.1, in sodium sulphite, 0.025M in N, N, N¹, N¹-tetramethyl-p-phenylenediamine dihydrochloride and 3% in agar. The green pigment Acramin Green F3G was also included in the cell with a transparent tin oxide cathode and a silver anode. The cell was cycled on 1.5 volts.

The cell was cycled for 1000 times at the above voltage with the forward current being applied for 0.5 seconds and the clearing current for 1.0 seconds.

At this state the cell cleared only in patches, but after resting the cell for 24 hours a further 500 cycles were possible before the same phenomenon recurred. On resting again, the cell again functioned as before.

Note that this cell was not designed to function with continuous cycling. This was indicated earlier in the light reflectance measurements. A better method of testing this particular cell would be to perform one cycle and then rest for a few seconds, this process then being repeated. However, this has so far not been practical.

APPENDIX 3

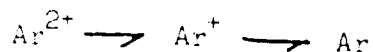
THE EFFECT OF ORGANIC SOLVENTS AND TEMPERATURE

Organic Solvents

The possibility of carrying out redox reactions in organic solvents was partially investigated. Several solvents were tried with poly-N,n-butylene-4,4'-bipyridinium dibromide(I) as the redox compound.

The first solvent tried was dimethylformamide, but compound(I) was found to be insoluble in this. The addition of a little methanol to the dimethylformamide rendered compound(I) partially soluble. In the presence of hydroquinone as adjunct this system gave a pale purple colour at the cathode when 2 to 3 volts were applied between a tin oxide transparent cathode and a silver anode. Prolonged application of the current resulted in the pale blue colour turning to a pale yellow colour. The cell could be reversed through both colour changes.

The above observations are in agreement with the literature which states that the reaction,



is reversible in organic solvents. (Note that the second reduction is reversible in organic solvents, but is not in water.) In addition, the reduced species formed at the cathode does not plate out on the cathode as is the case in aqueous solution. In fact the one electron reduction product, Ar^+ , is reported to be soluble in organic solvents with the result that only pale colours form at the cathode.

Other solvents tried were ethanol, 2-methoxyethanol, ethylene glycol dimethyl ether anhydride. In all these solvents compound(I) was found to be virtually insoluble.

Solvents with high dielectric constants have been suggested for use with redox systems. Two such solvents were tried; viz., glycerol and ethylene glycol.

A cell was made containing compound(I), hydroquinone and tetramethyl ammonium bromide as supporting electrolyte in glycerol. Various potentials were applied between a tin oxide transparent cathode and a silver anode. A pale purple colour formed at the cathode at a voltage of about 2 volts, but a potential of 3 volts produced a pale yellow colour.

The use of ethylene glycol instead of glycerol in the above system gave a better response. At a voltage of about 1 volt the purple colour was formed at the cathode in greater intensity. The colour was still paler than that obtained in aqueous solution, however. At voltages greater than 2V the purple colour changed to yellow. Both colour transitions were reversible.

It was found that gels could be made with polyvinyl alcohol and ethylene glycol. A gel which contained polyvinyl alcohol (10g) in ethylene glycol (100mls) produced a good gel, as did a gel which contained polyvinyl alcohol(10g) in ethylene glycol (75mls) and water (25mls). Increase in the water content above 25% resulted in non-gelling of the solution.

It was shown that the colour changes produced in liquid ethylene glycol could be produced in both the gels mentioned above. It is interesting to note that the presence of water (25%) in the gel did not result in the plating out of the one or two electron reduction products as was the case in aqueous solution. In addition, the depth of colour produced remained the same as that produced in the liquid ethylene glycol.

During the course of experiments it was also shown that the system employing the sodium salt of 2:6-anthraquinone disulphonic acid and potassium ferrocyanide also functioned in an ethylene glycol/polyvinyl alcohol gel at an applied voltage of 3 volts.

Effect of Temperature

The effect of temperature on the action of two cells was briefly investigated. These cells consisted of gels which were:

(a) 5% in poly-N,n-butylene-4,4'-bipyridilium dibromide.

0.1M in sodium sulphite.

0.25M in N,N,N',N'-Tetramethyl-p-phenylenediamine dihydrochloride.

3% in agar.

This cell also contained the green pigment Acramin Green F3G, a tin oxide transparent cathode and a silver anode.

(b) 0.25M in the sodium salt of 2:6-anthraquinone disulphonic acid.

0.1M in potassium ferrocyanide.

1% polyvinyl alcohol in 75% ethylene glycol and 25% water.

Two tin oxide transparent electrodes were used in the cell with an applied voltage of 3 volts.

The effect of temperature in both of these cases was generally the same. At 0°C both still changed colour, but were fractionally slower than at room temperature. Conversely, on heating to 60°C the colour changes appeared to be fractionally quicker.

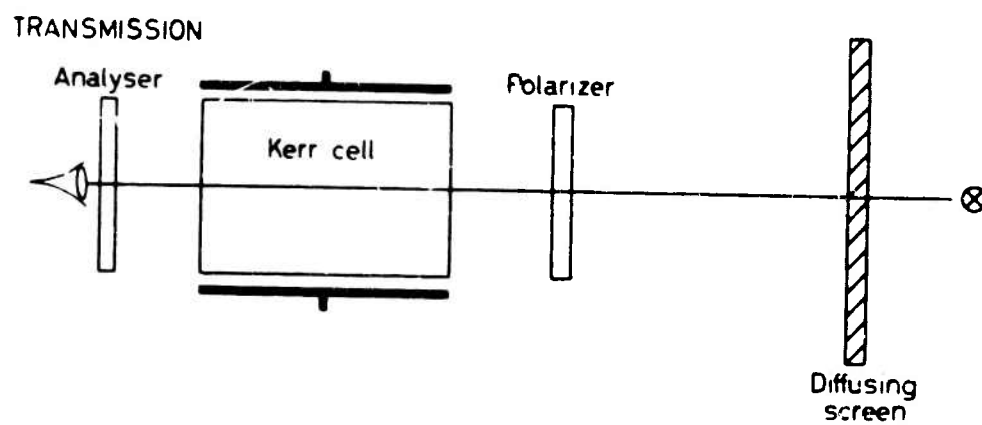


Fig. 1

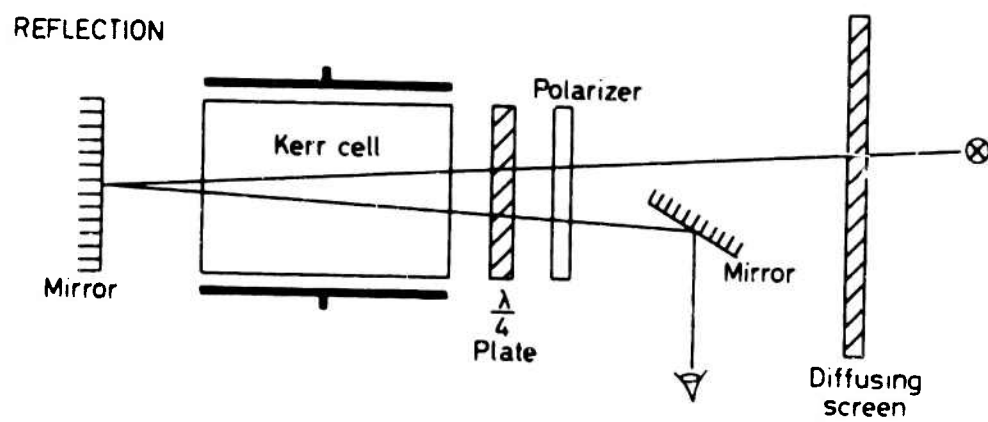


Fig. 2

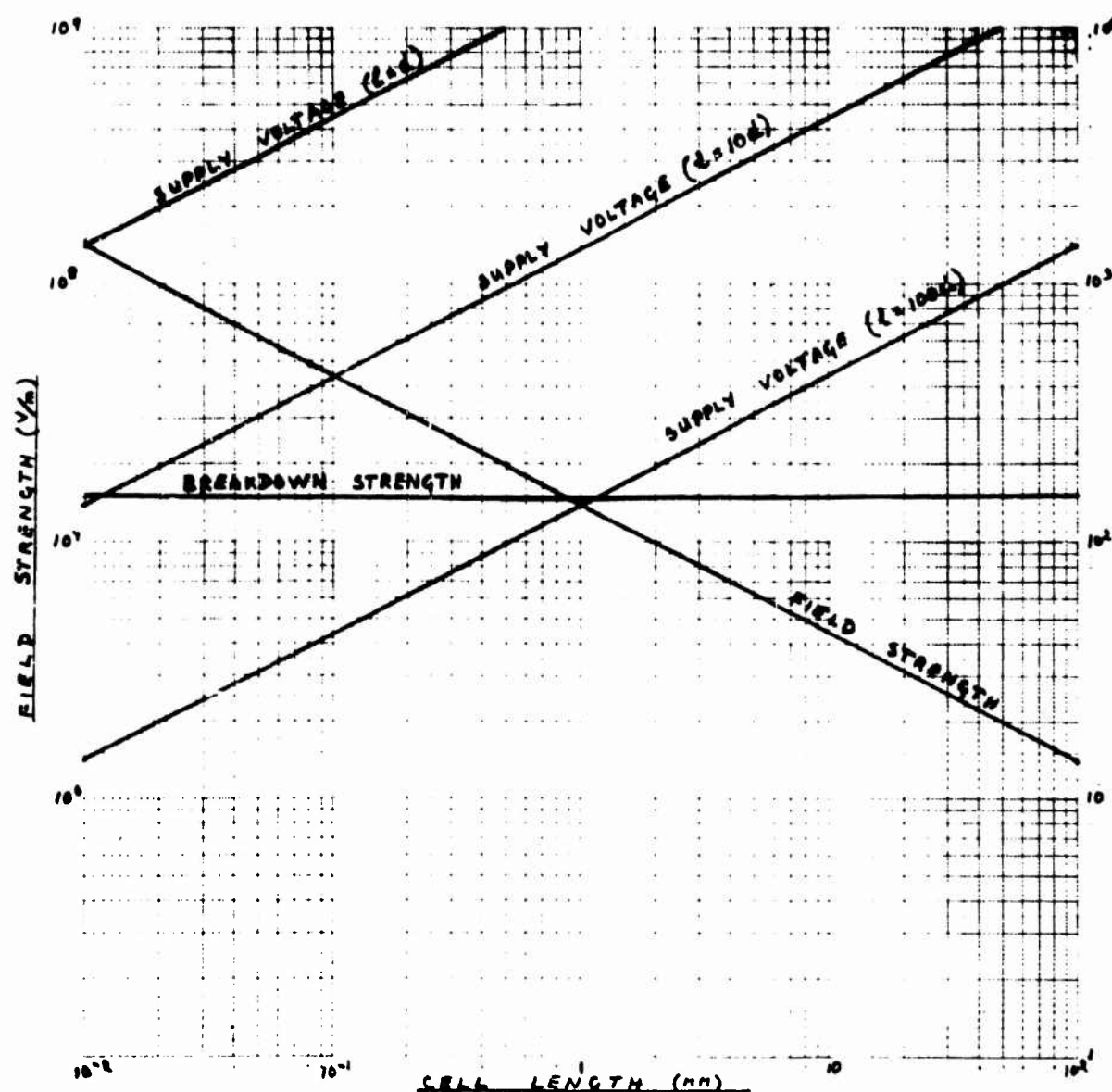


Fig. 3 Kerr-cell specification parameters.

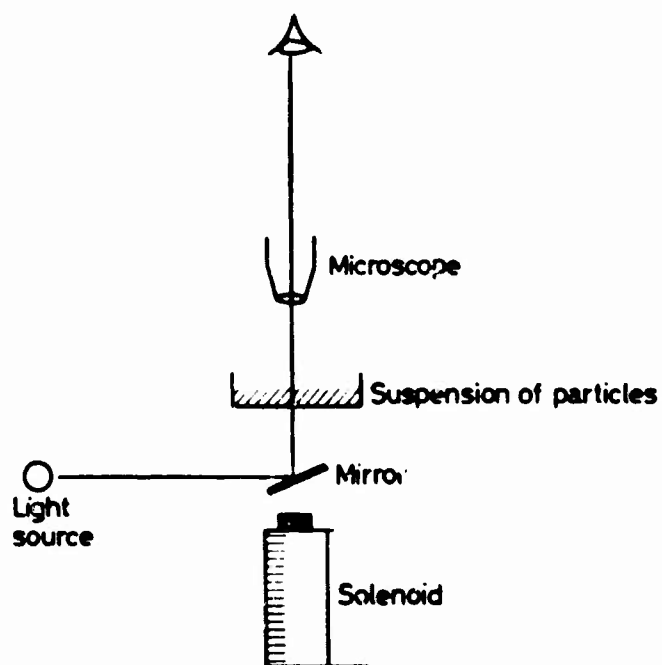


Fig. 4 Apparatus for electromagnetic shutter

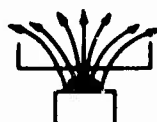


Fig. 5 Theoretical magnetic field

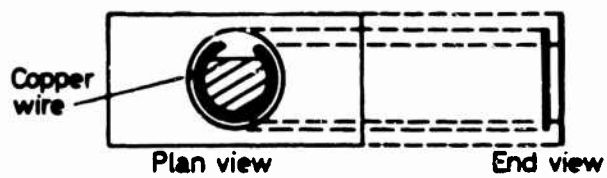


Fig. 6 Vertical cell



Fig. 7 Electroplating cell

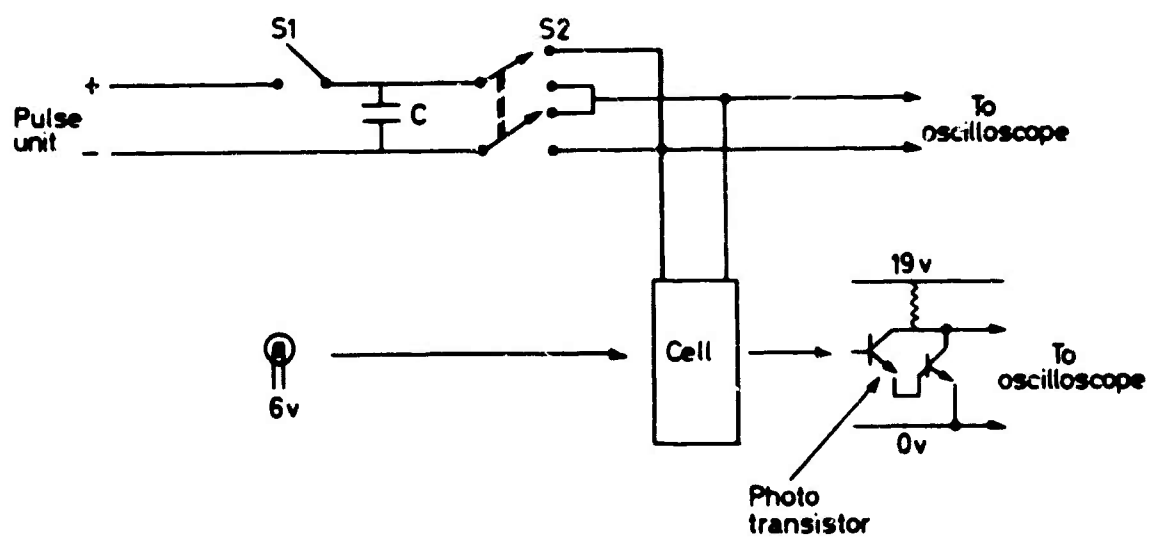


Fig. 8 Circuit diagram for electroplating experiment

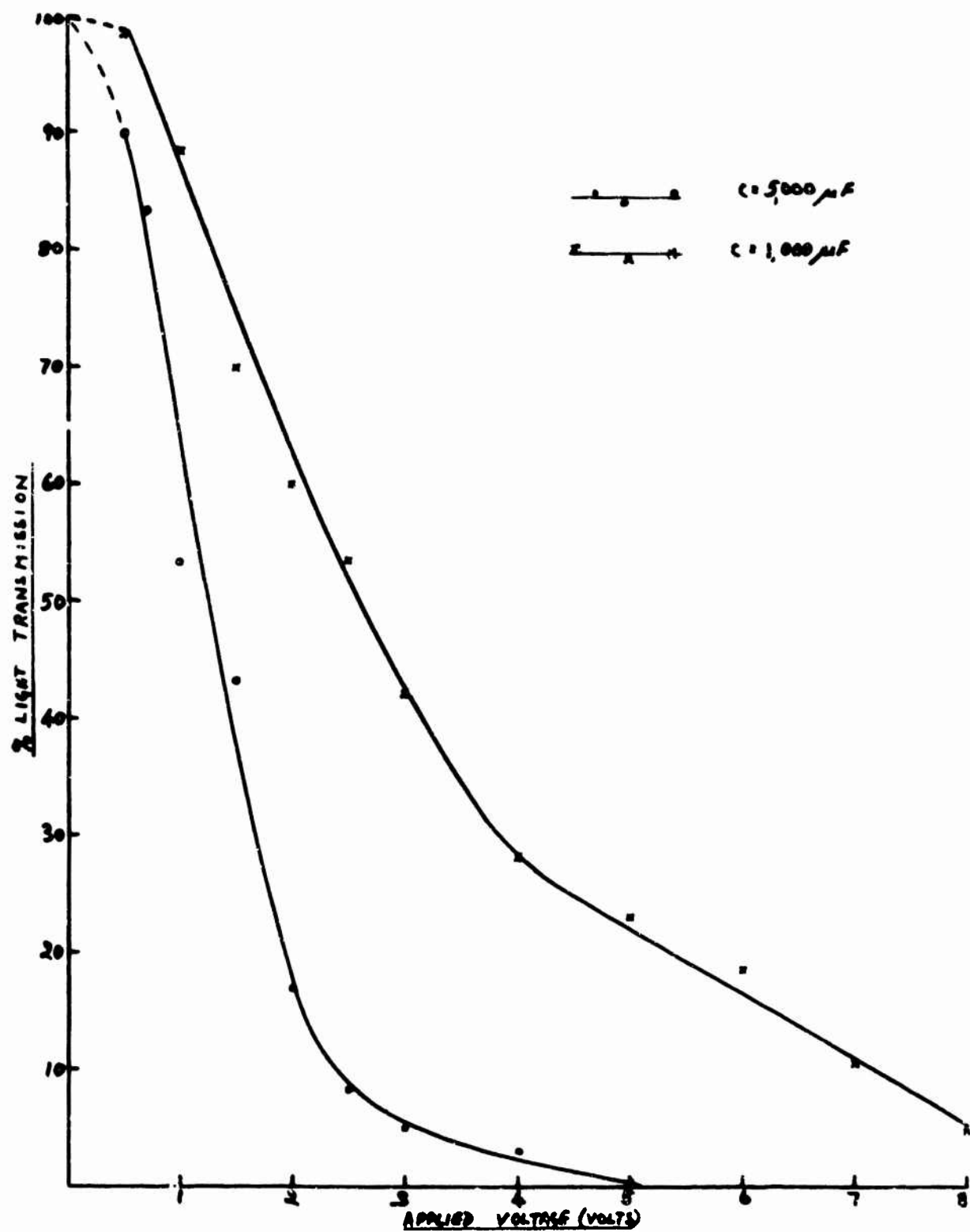
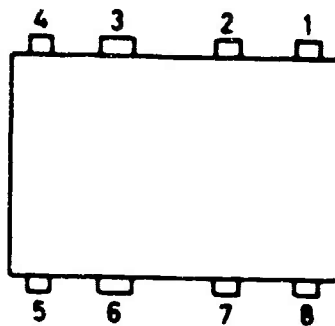


Fig. 9 Light transmission as a function of applied voltage.



TOP VIEW (8 pin dip package)

Pin Configuration

- 1 Ground
- 2 Trigger
- 3 Output
- 4 Reset
- 5 Control voltage
- 6 Threshold
- 7 Discharge
- 8 Vcc

BLOCK DIAGRAM OF TIMER A

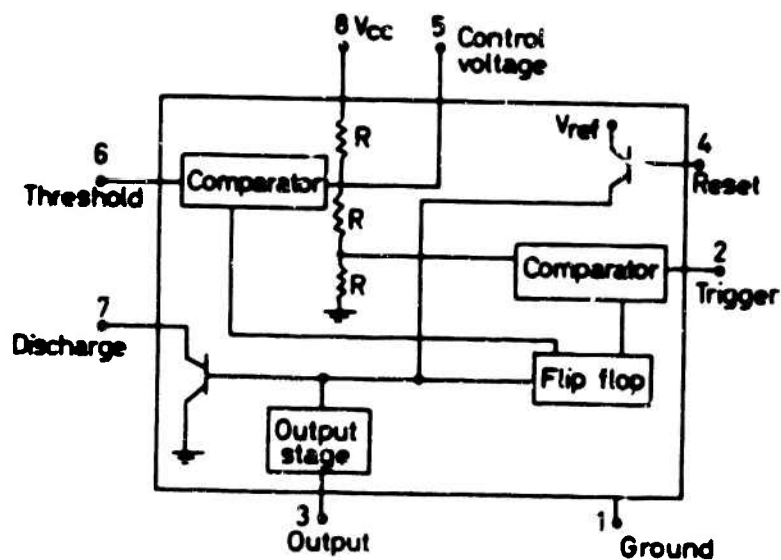


Fig.10 Block circuit diagram and pin configuration for timer A.

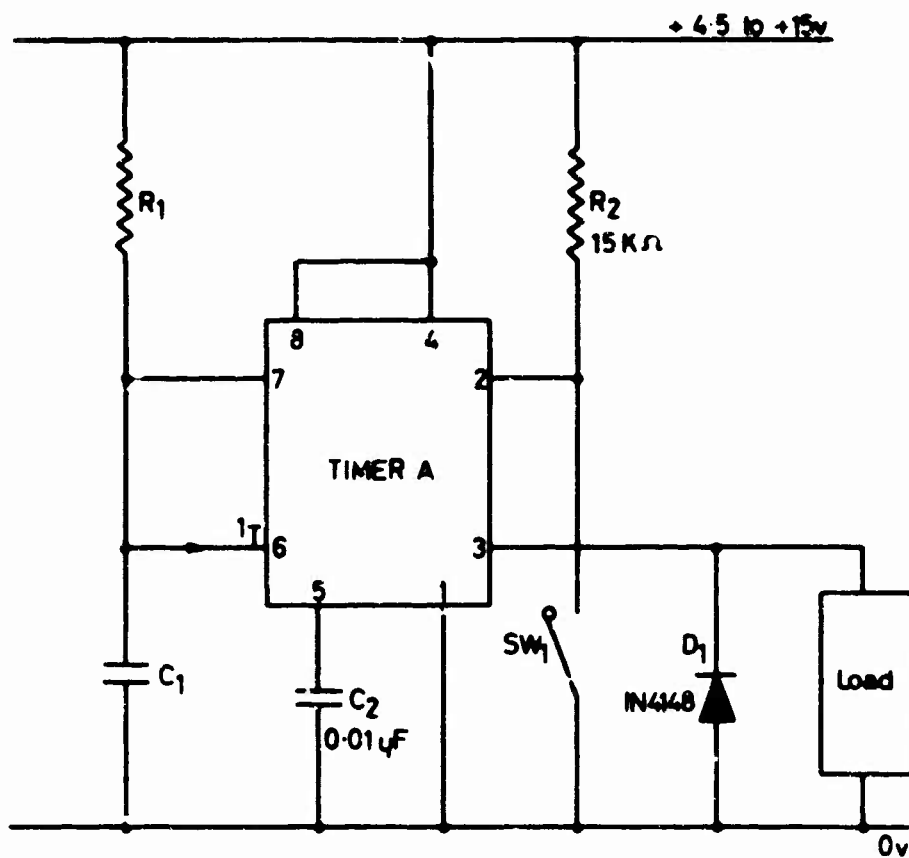


Fig.II Circuit diagram of one-shot pulse generator

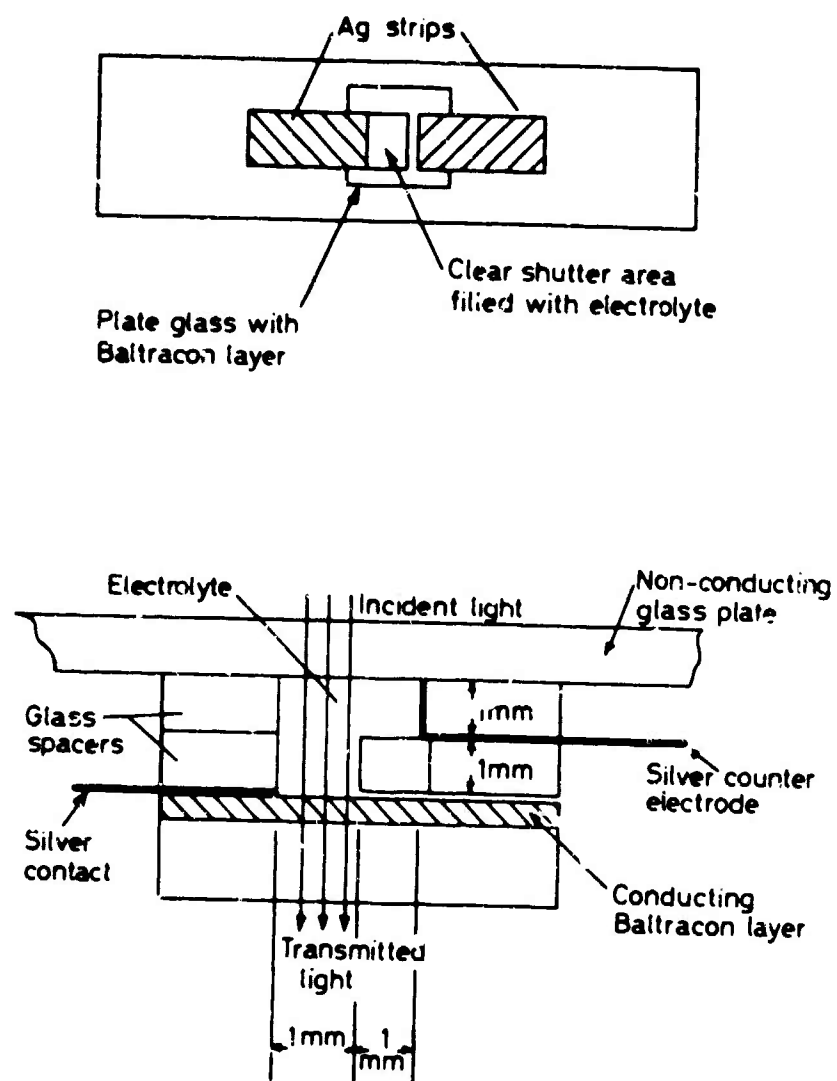


Fig.14 Reversible electroplating cell.

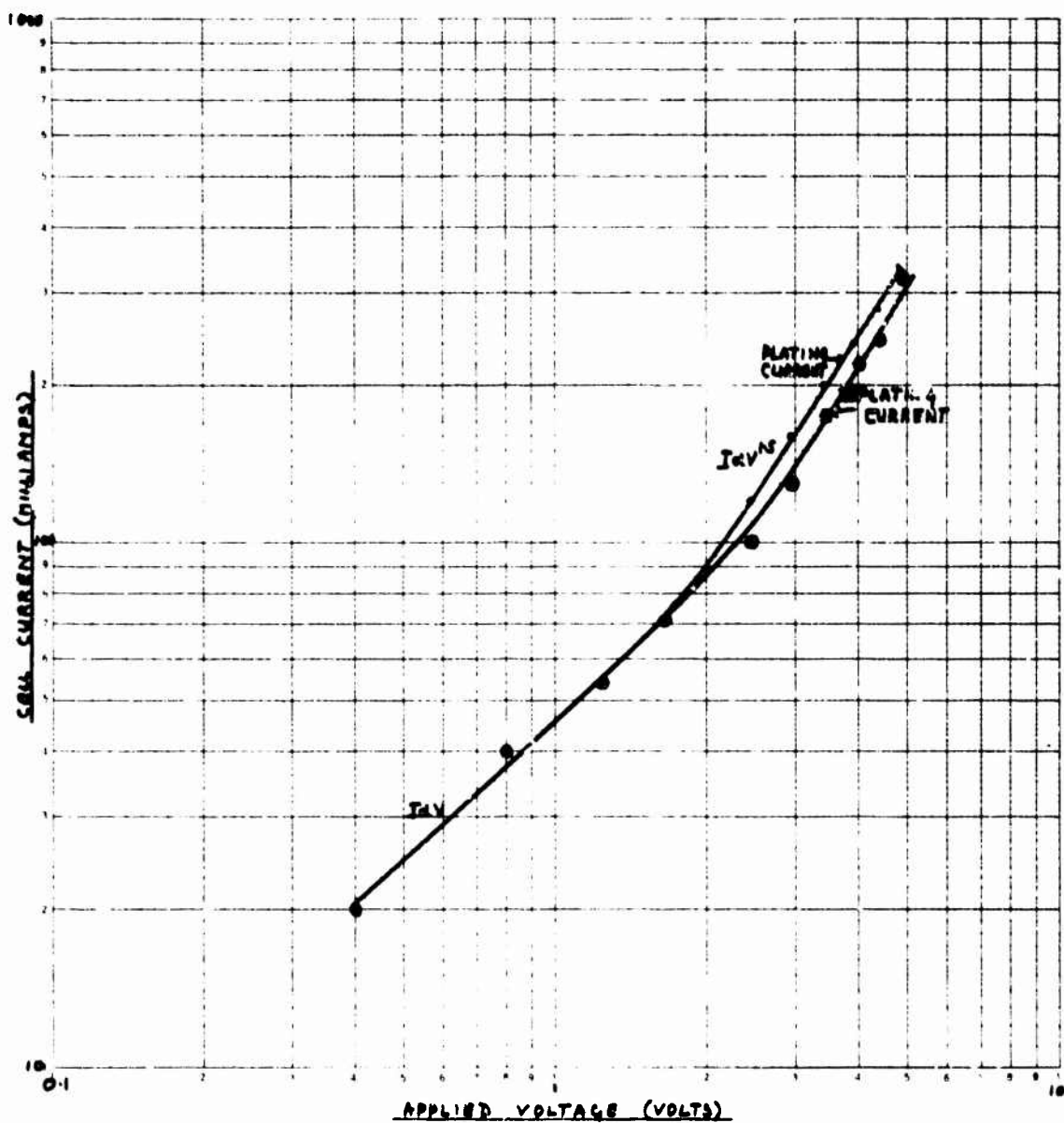
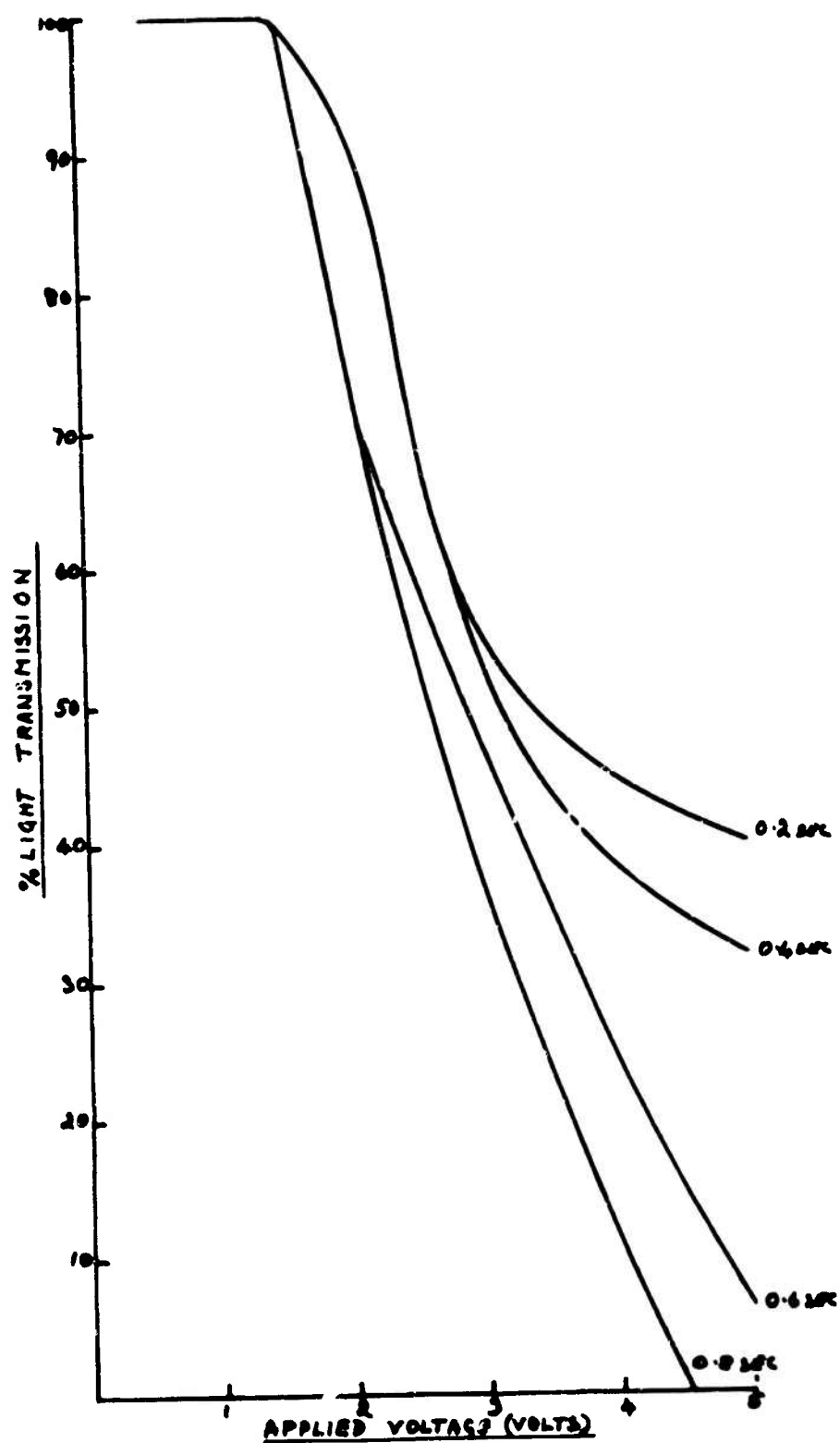


Fig. 15 Plating and deplating current-voltage curves in alkaline solution.



3. 16 Light transmission as a function of applied voltage and pulse width.

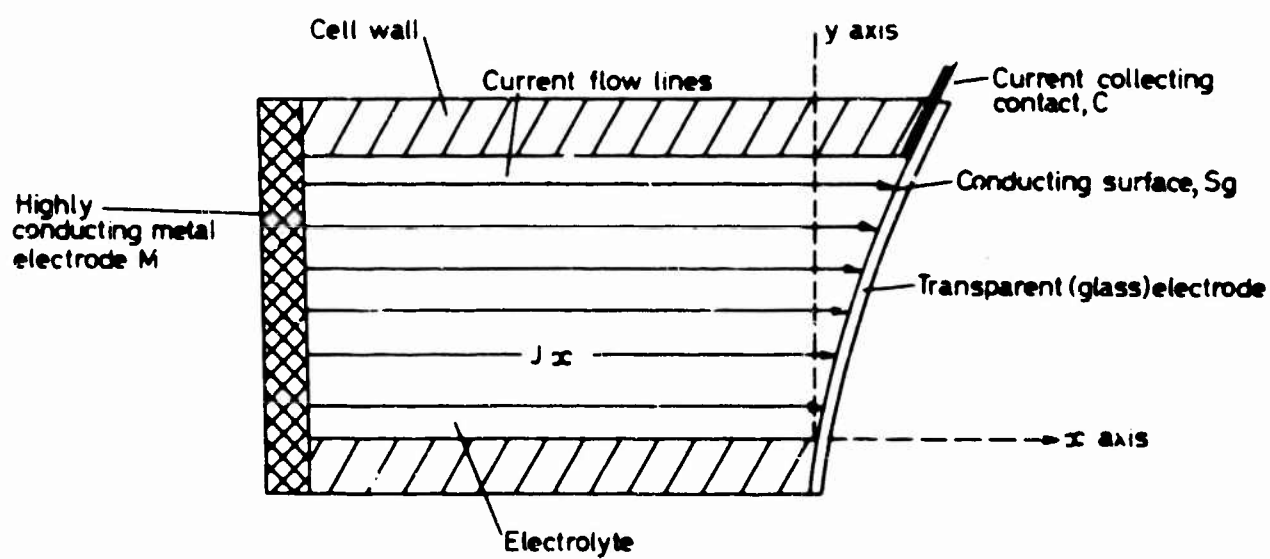


Fig.17 Plating cell with parallel current flow lines

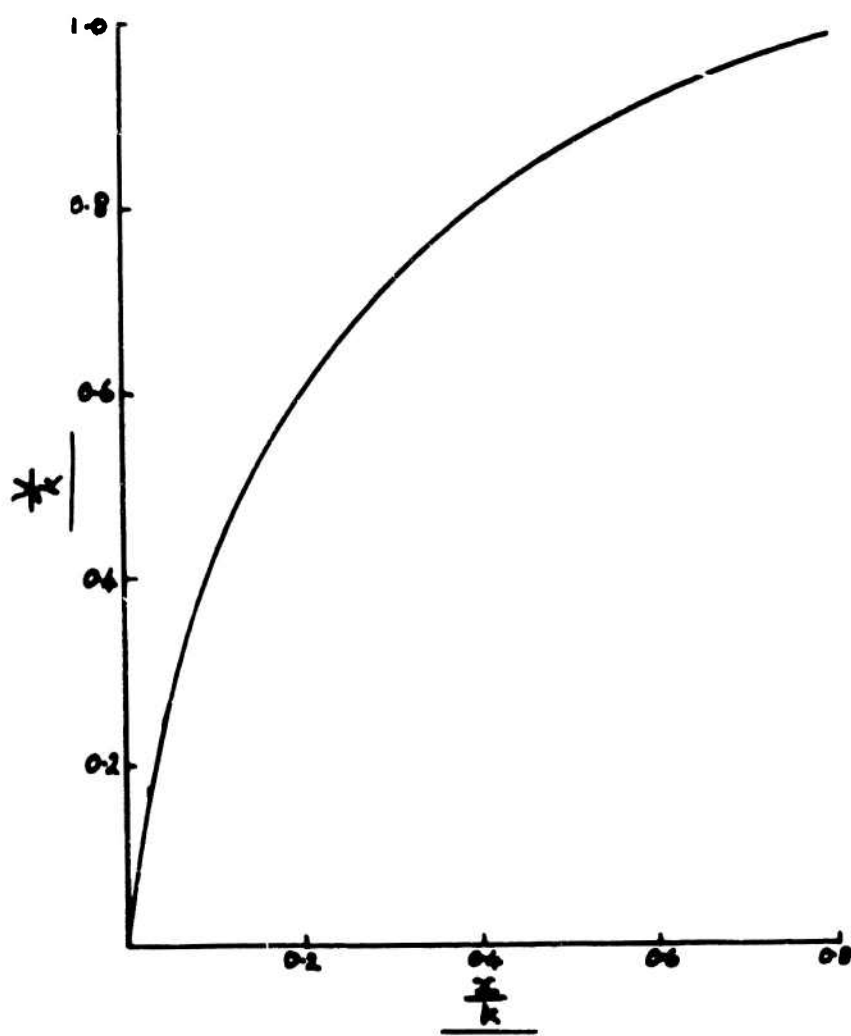


Fig. 18 Plot of equation 16.

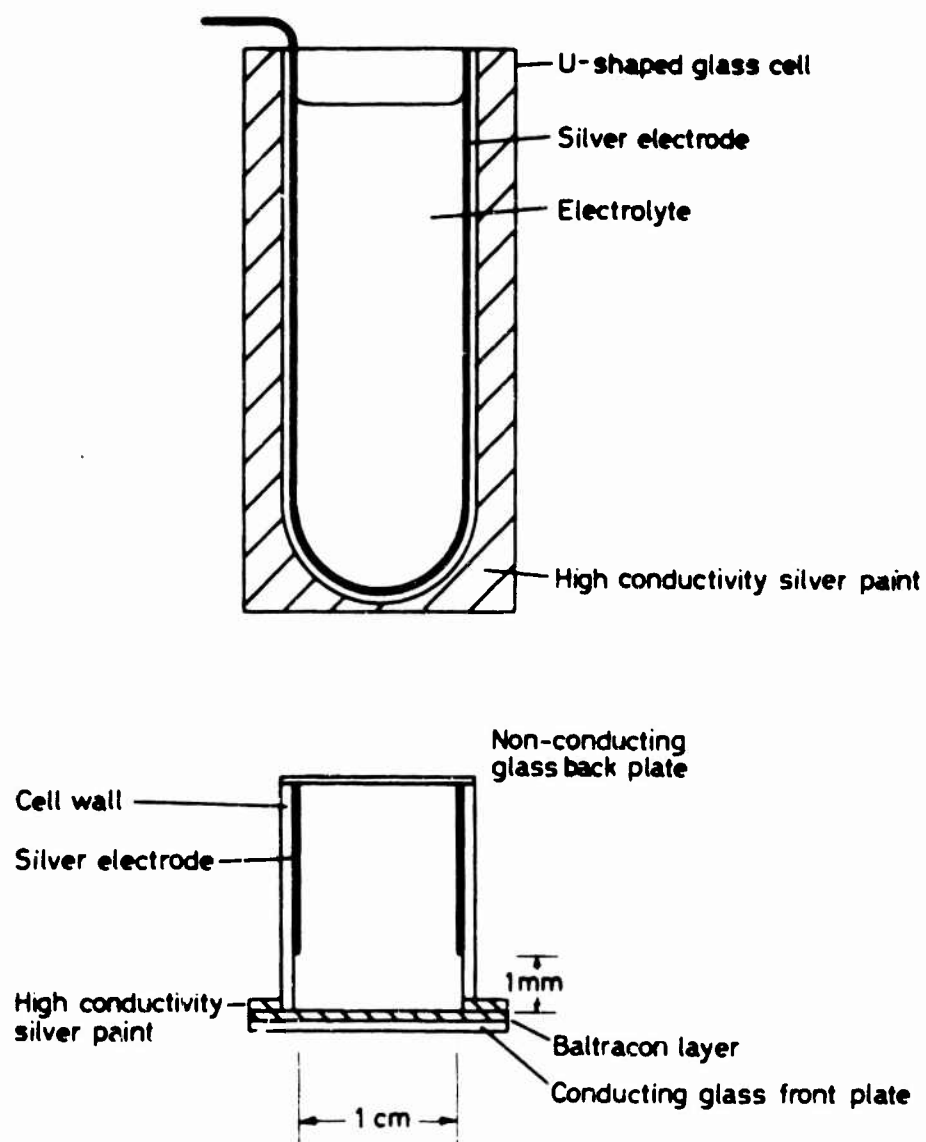


Fig.19 Large area reversible electroplating cell

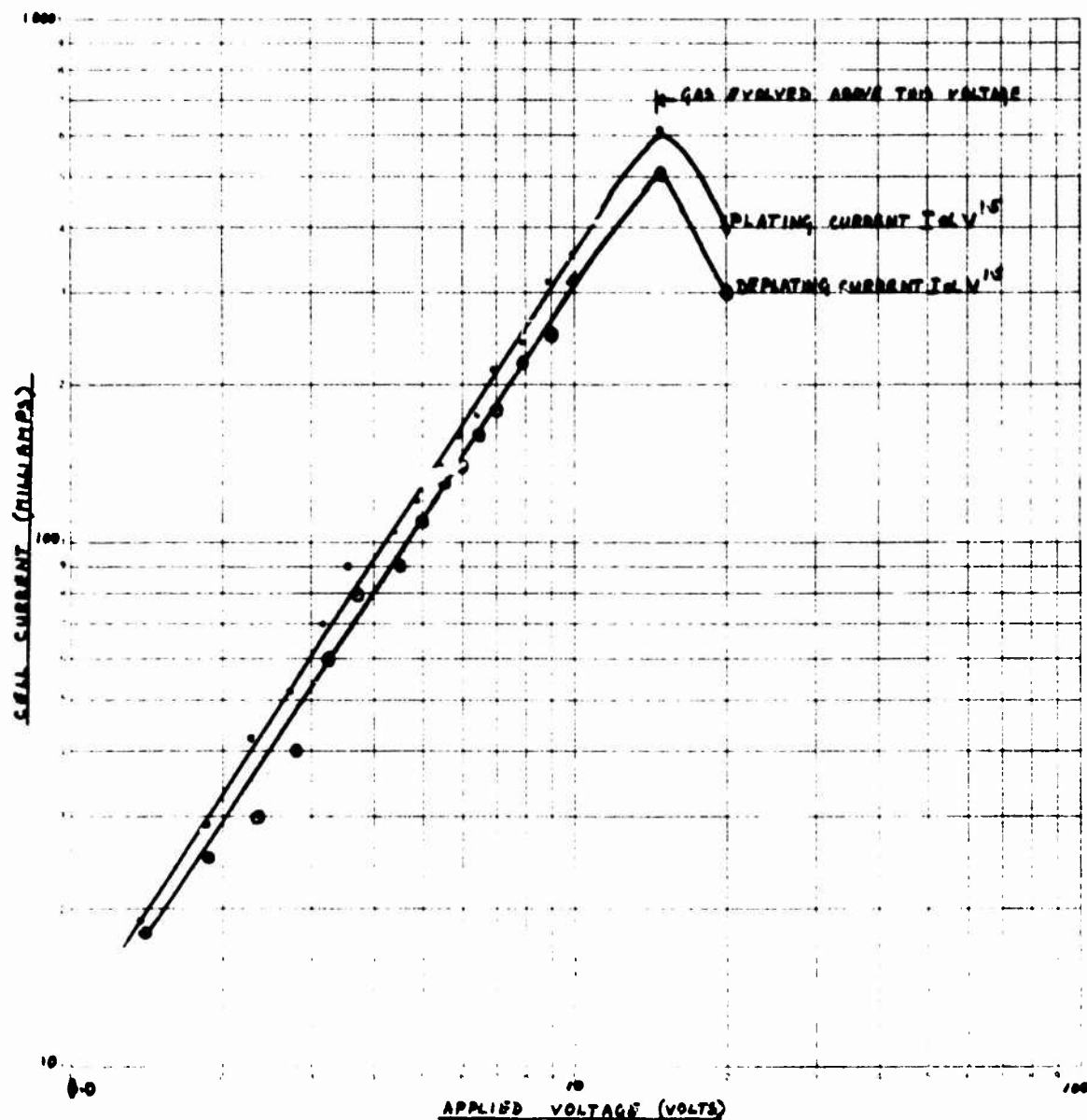


Fig. 20 Plating and deplating current-voltage curves in neutral solution with polyvinyl alcohol.

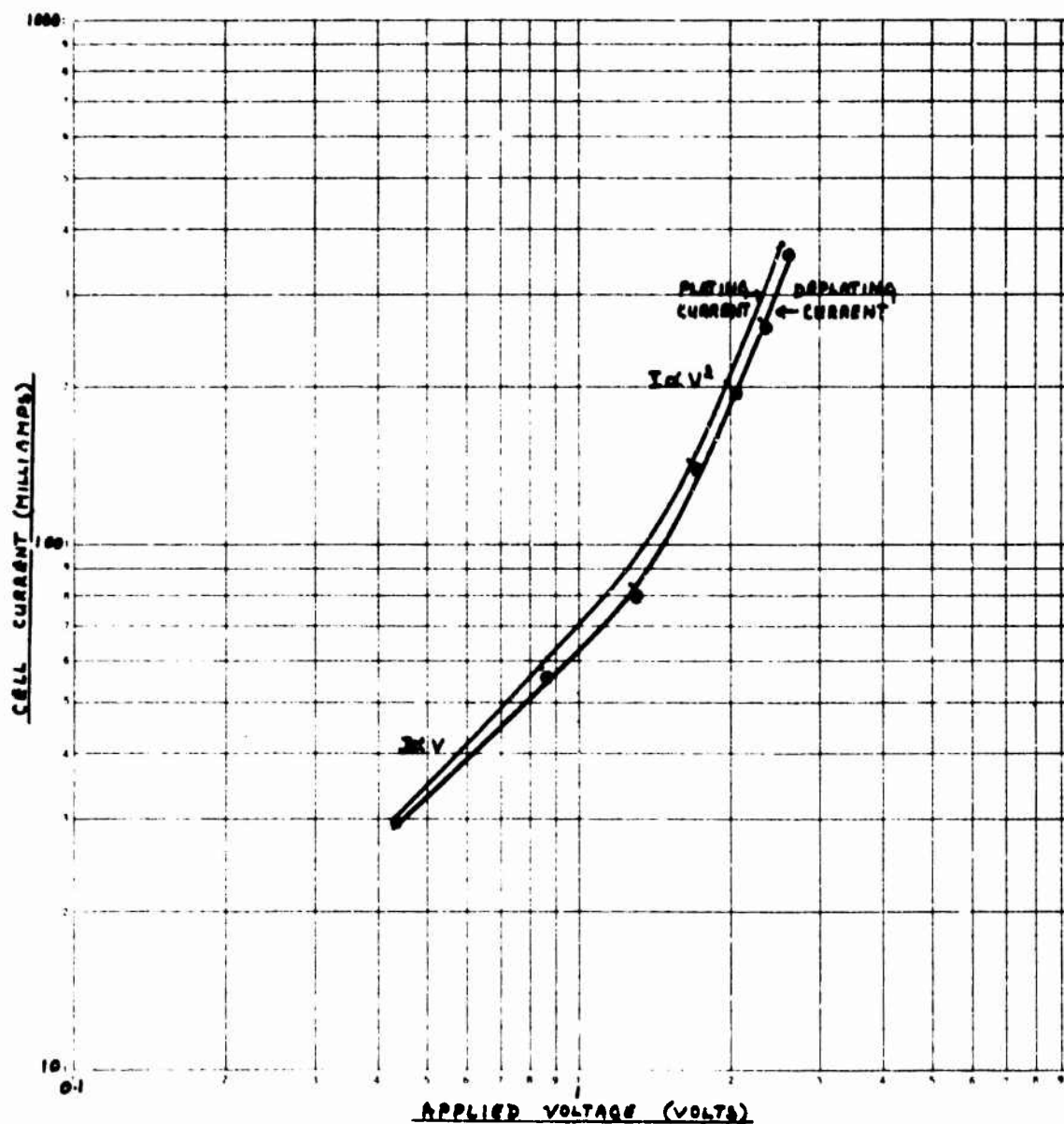


Fig. 21 Plating and deplating current-voltage curves in neutral solution without polyvinyl alcohol.

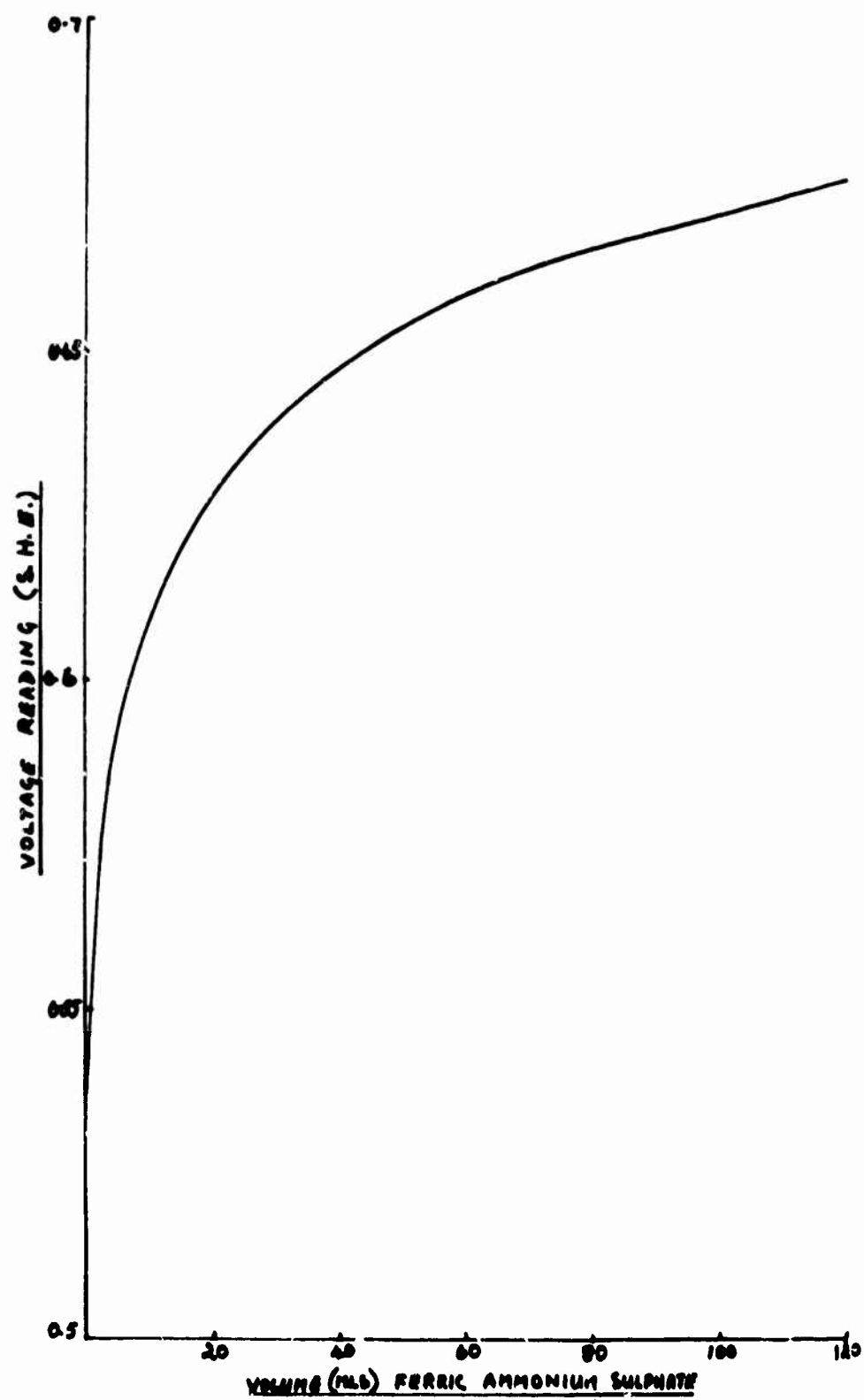


Fig. 22 Potentiometric titration curve for ferrous-ferric system.

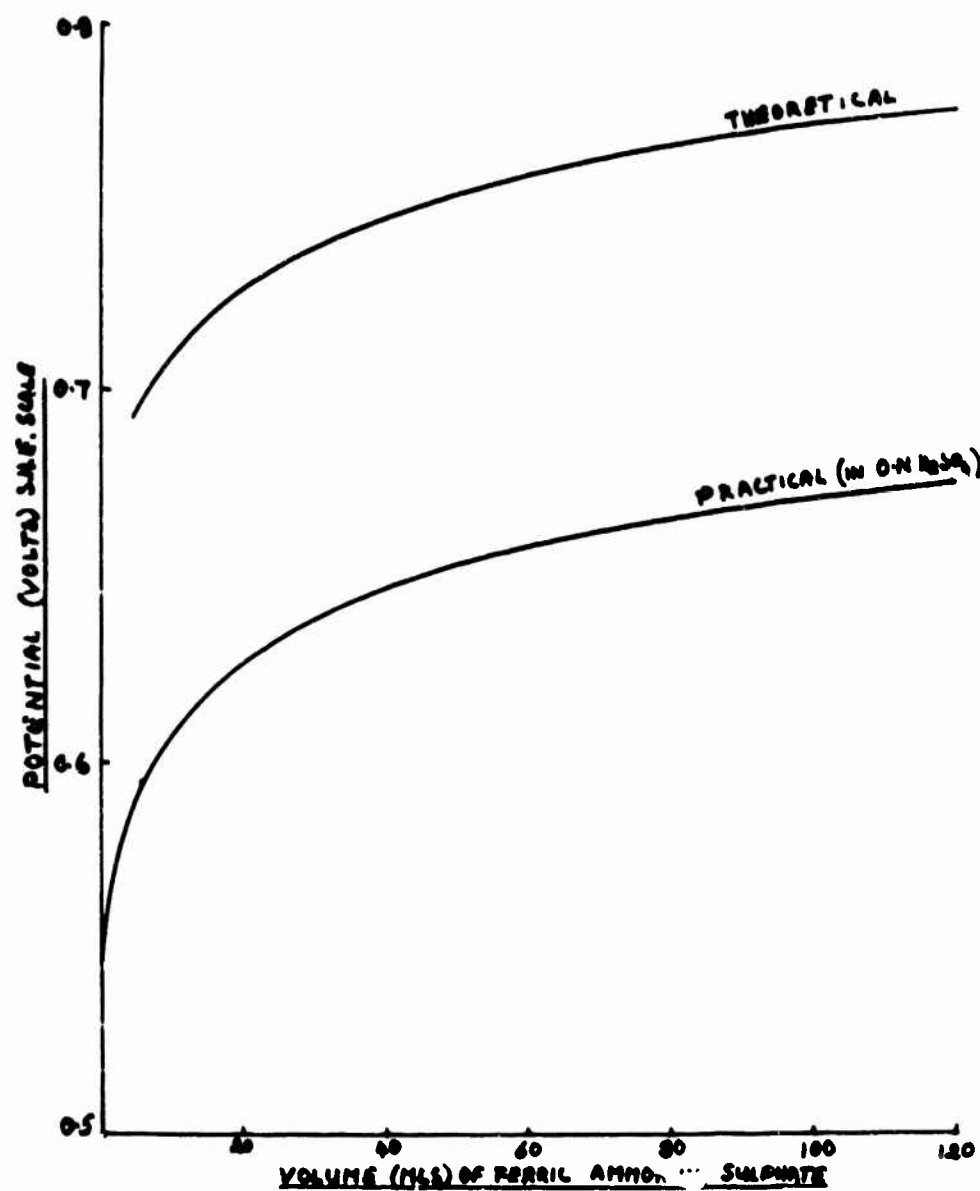


Fig. 23 Comparison of theoretical and practical potentiometric titration curves for ferrous-ferric system.

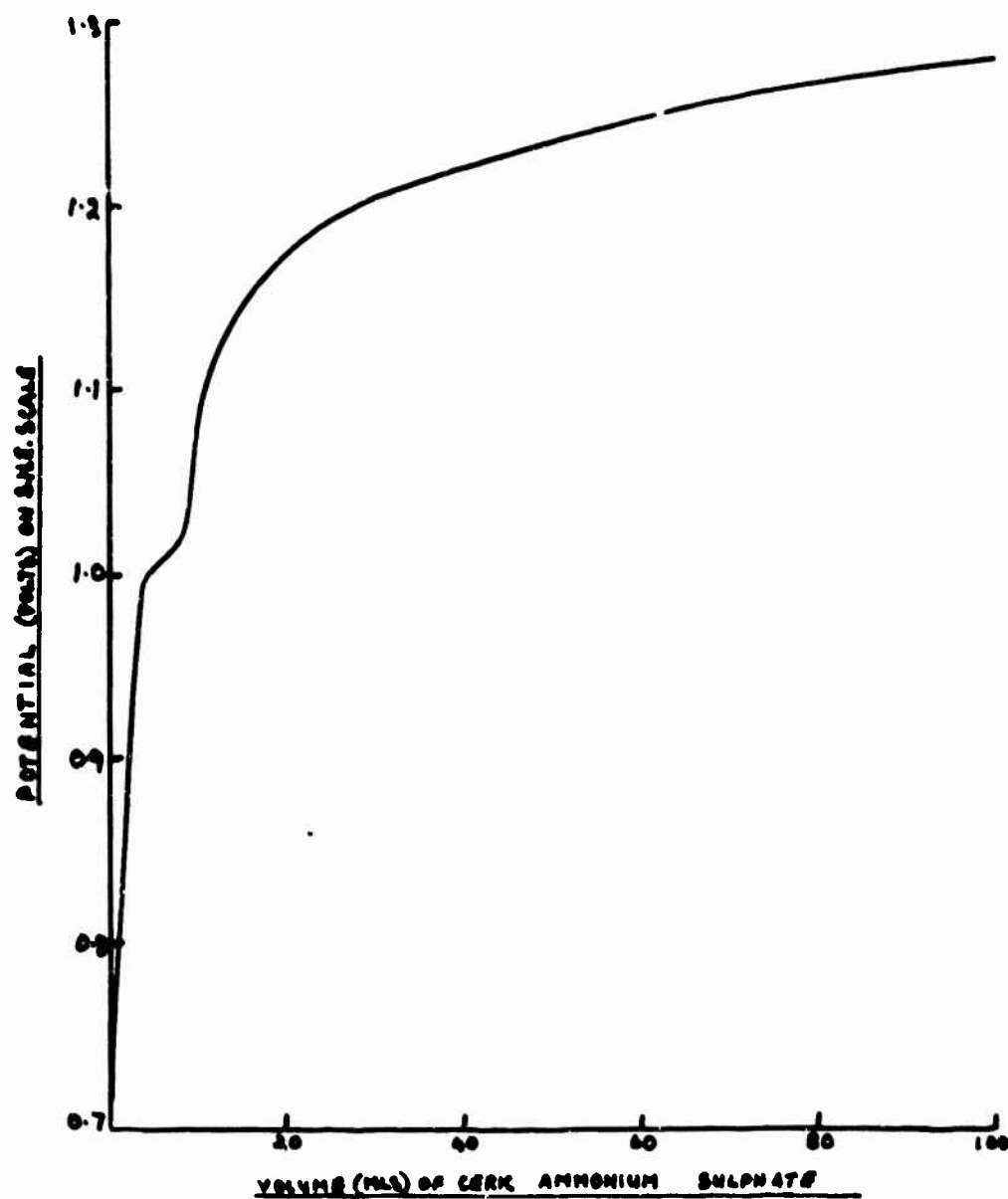


Fig. 24 Potentiometric titration curve for cerous-ceric system with Xylene Cyanol FF as indicator.

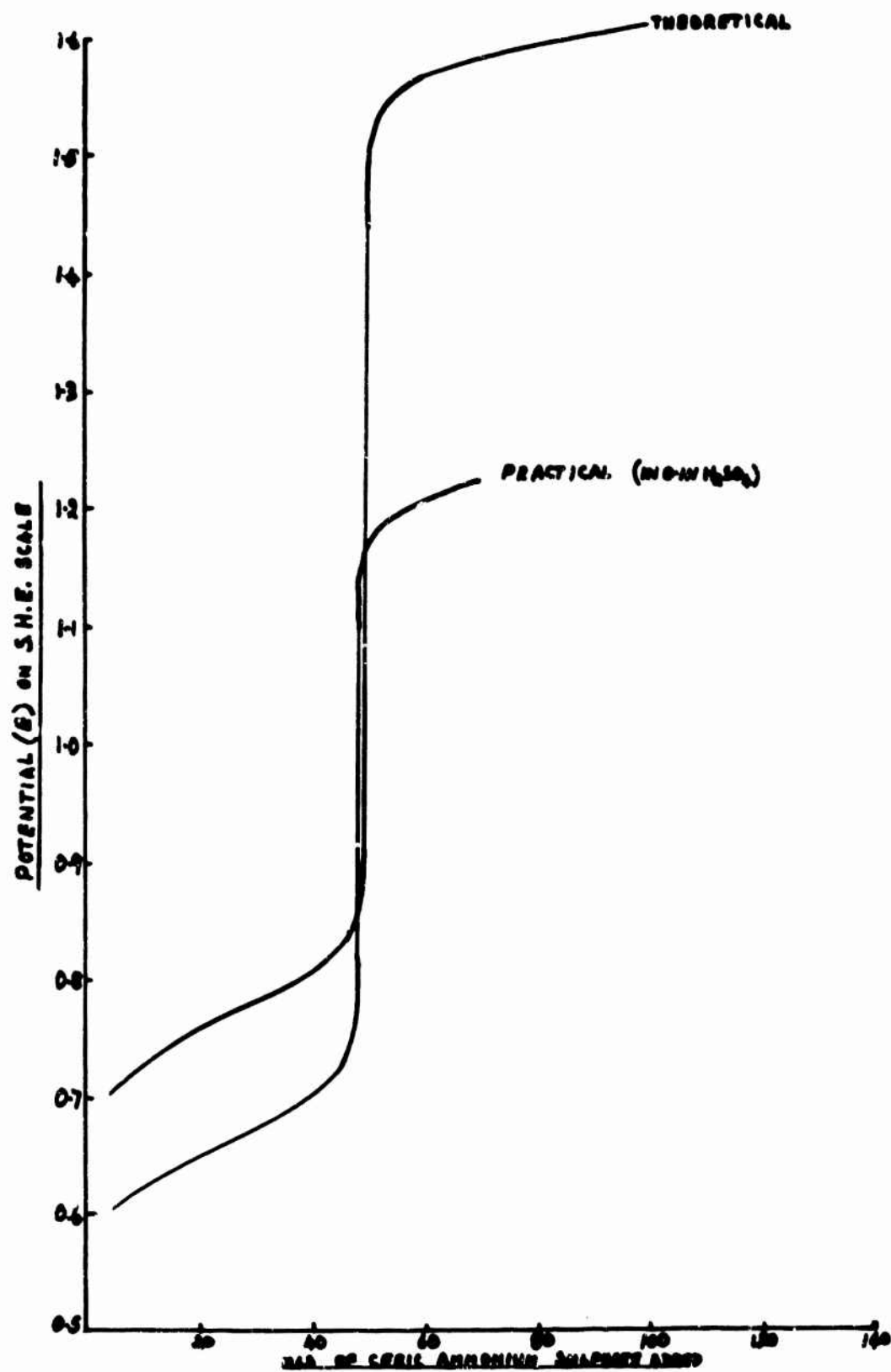
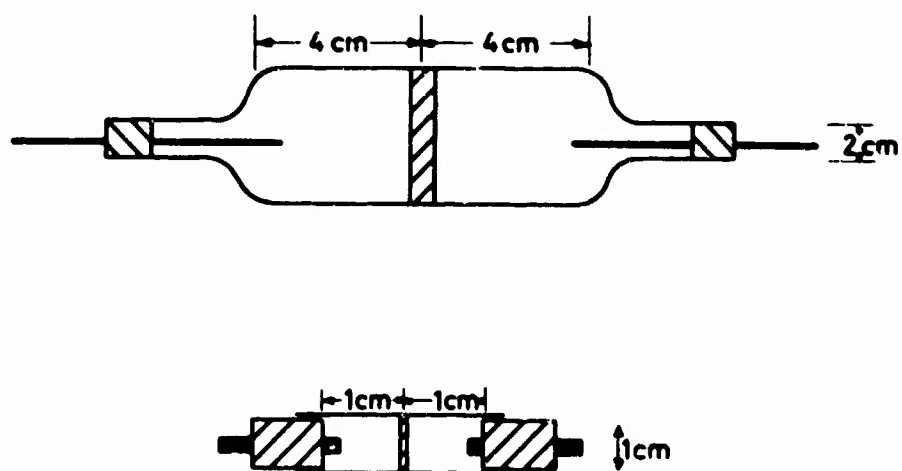


Fig. 25 Comparison of theoretical and practical potentiometric titration curves for the ferrous-ceric system.



Not to scale

Fig.26 Cells with sintered glass diaphragm

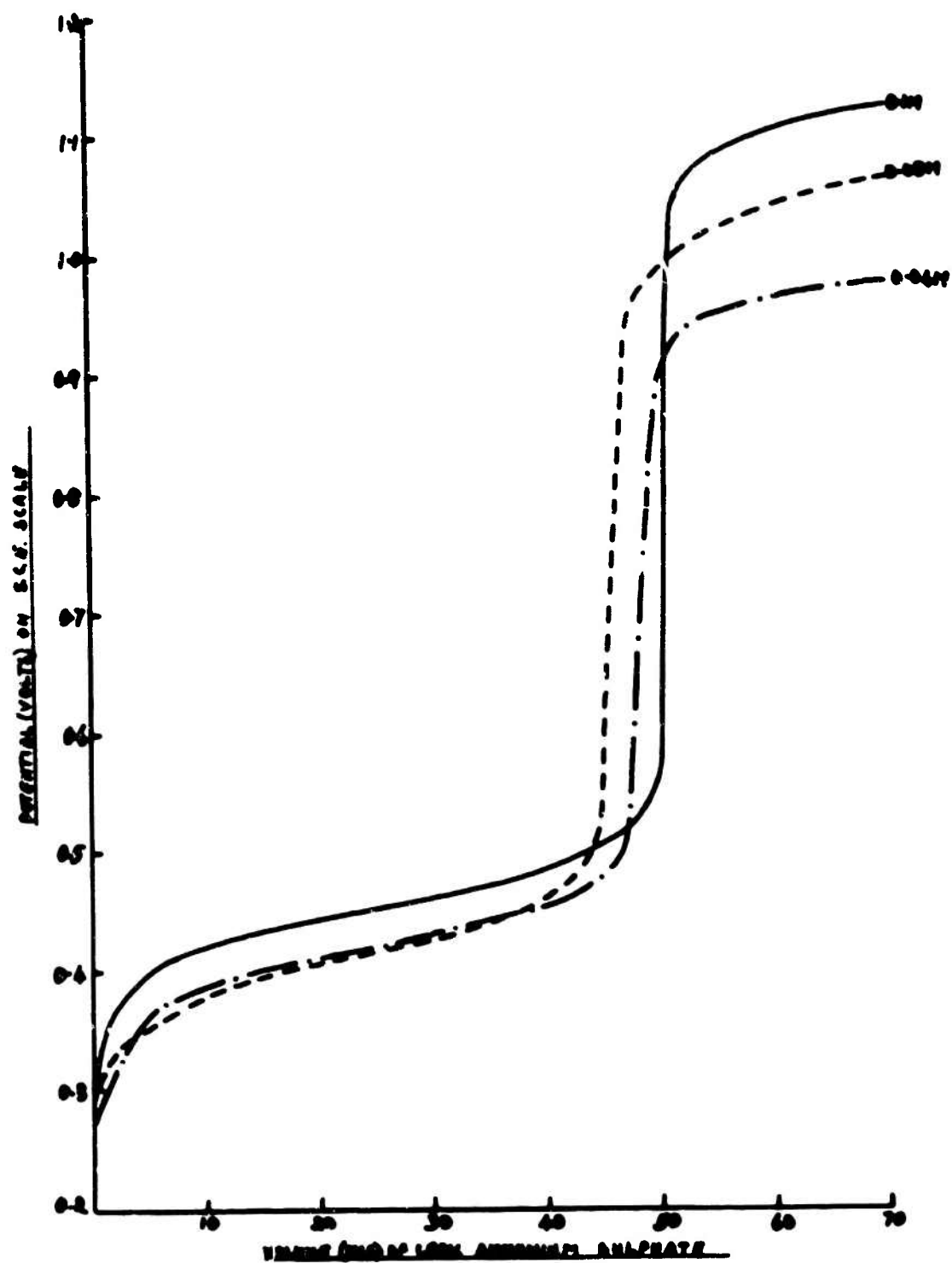


Fig. 27 Variation in potentiometric titration curve with concentration of reagents.

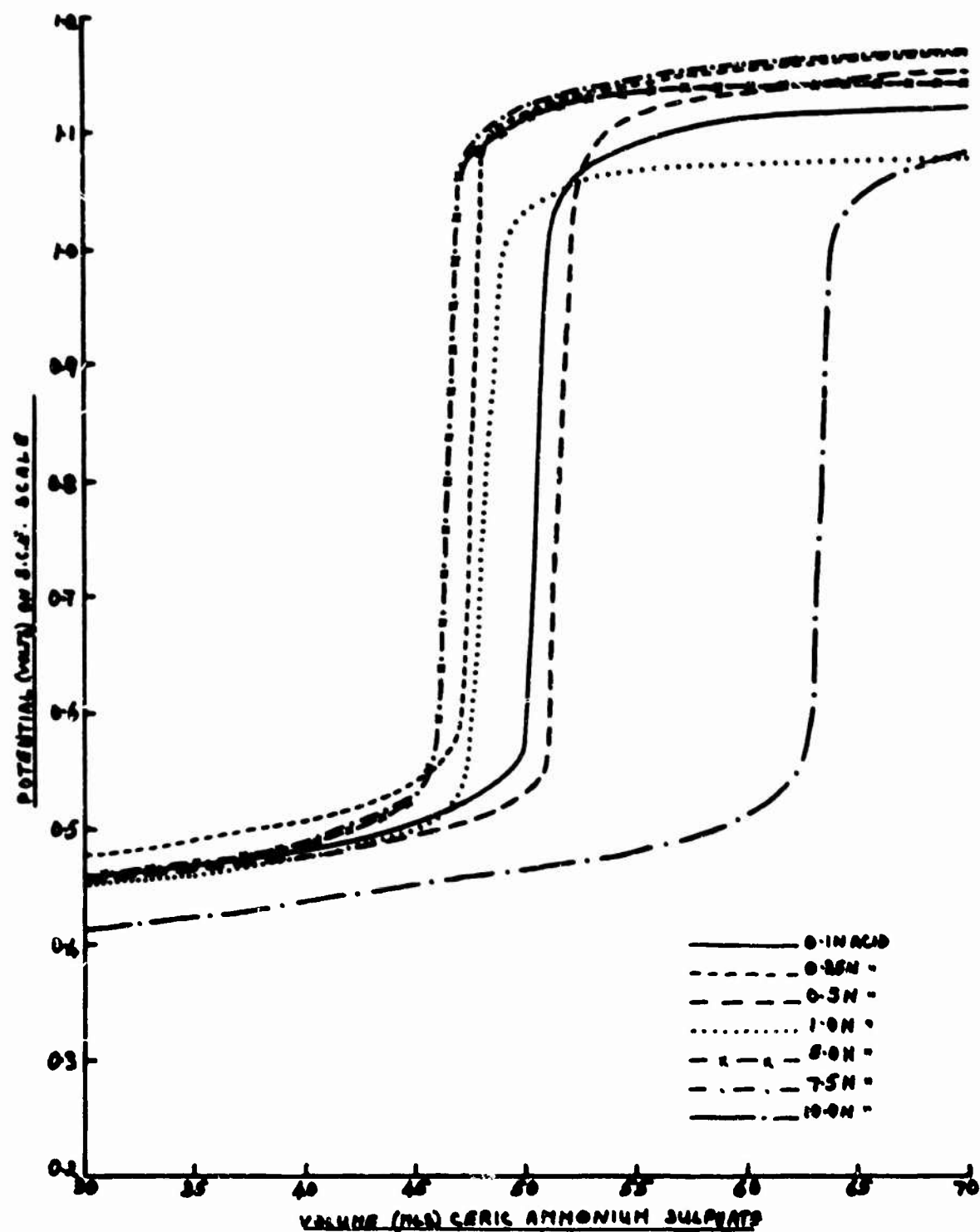


Fig. 28 Variation in potentiometric titration curve with acid concentration.

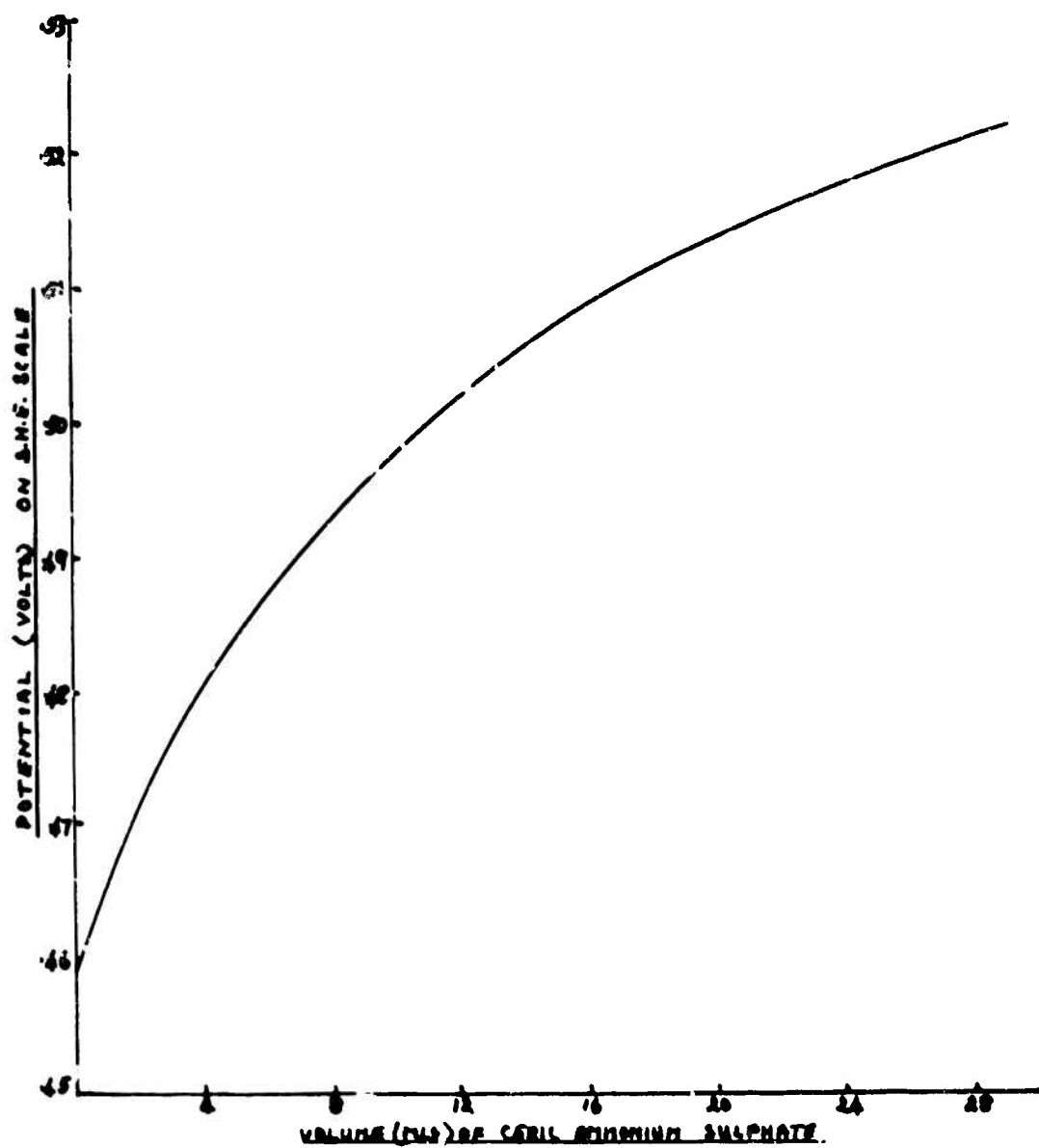


Fig. 29 Potentiometric titration curve for the ferrous gallate-ceric system.

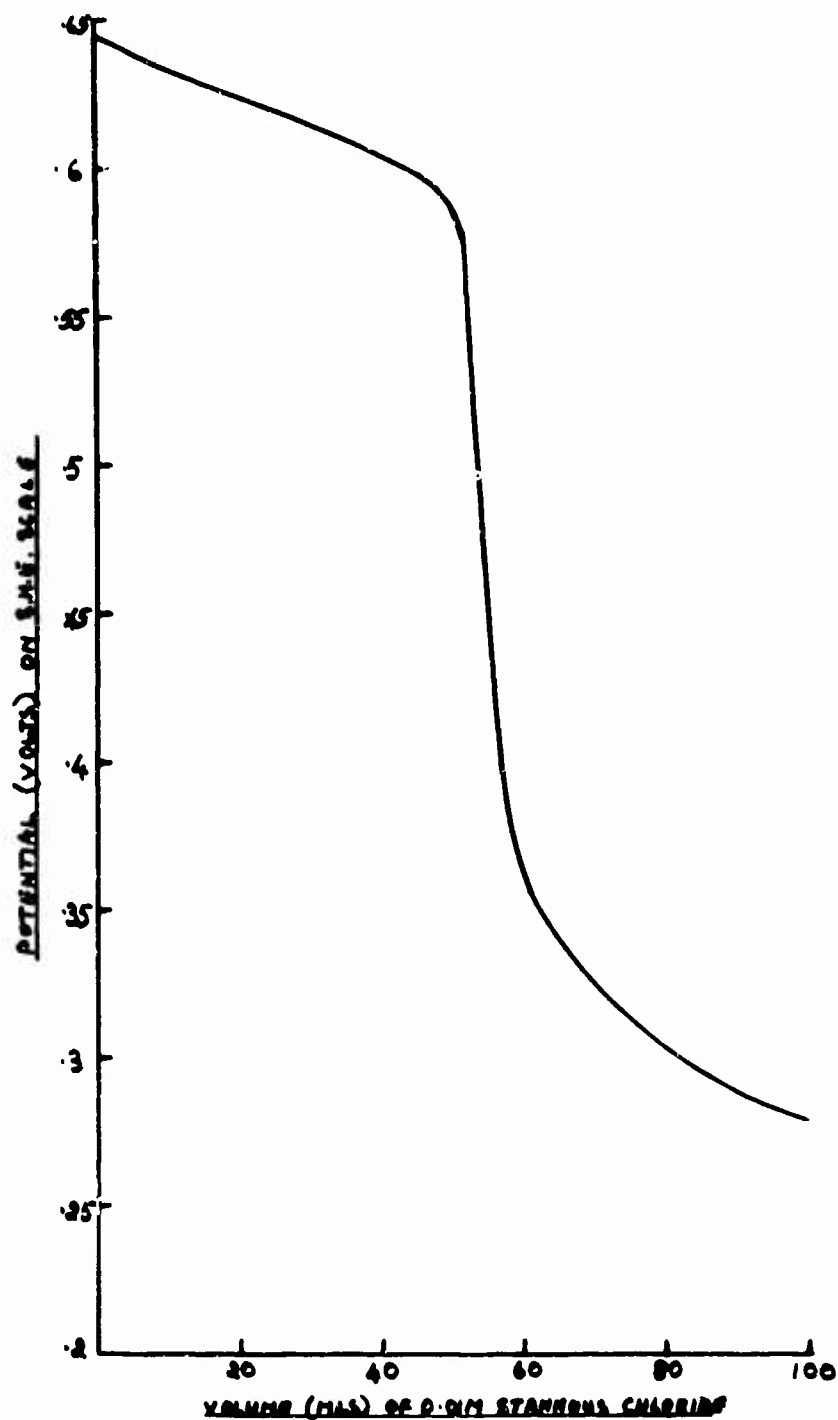


Fig. 30 Potentiometric titration curve for the stannous-iodine system.

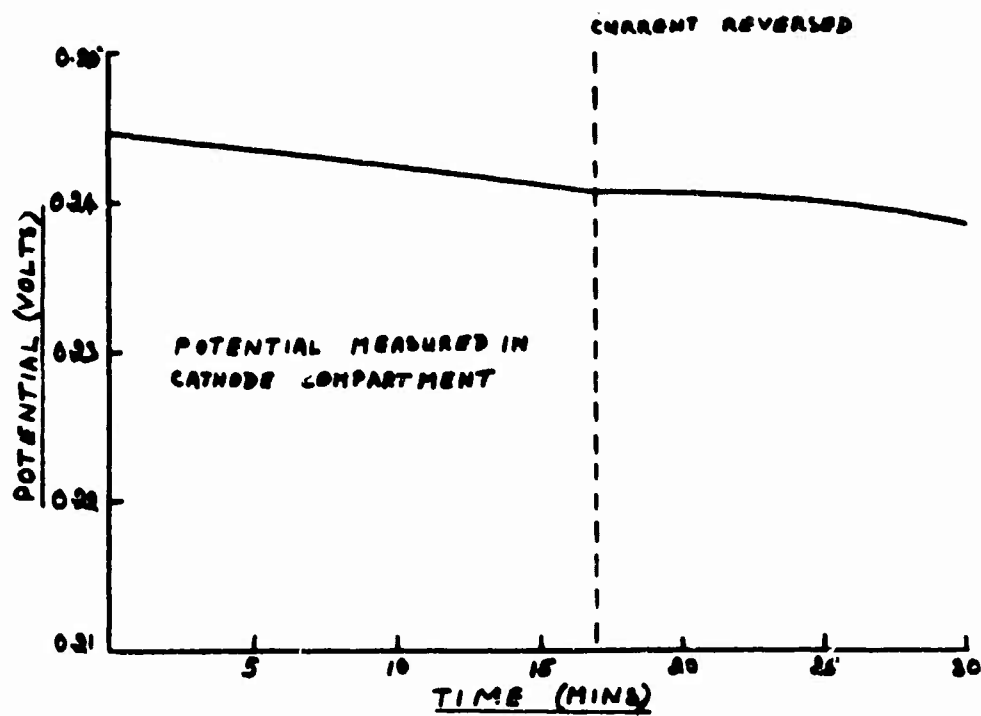


Fig. 31 Application of potentials via copper electrodes to the stannous-iodine system.

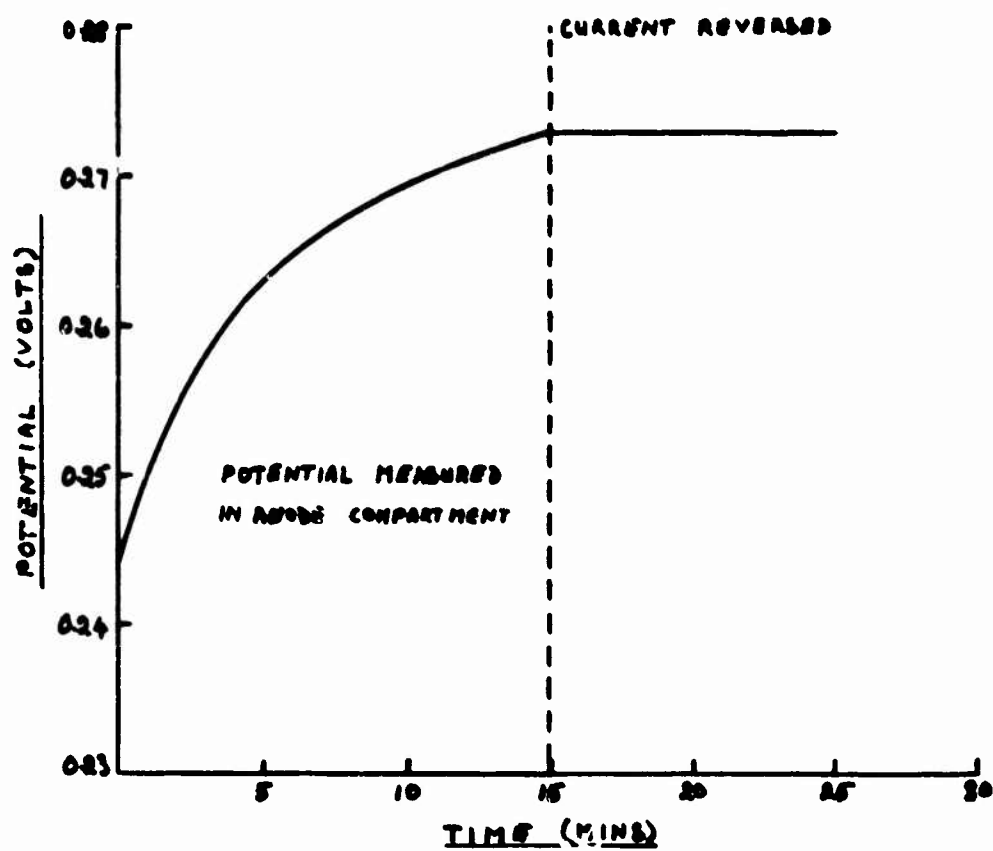


Fig. 32 Application of potentials via platinum electrodes to the stannous-iodine system.

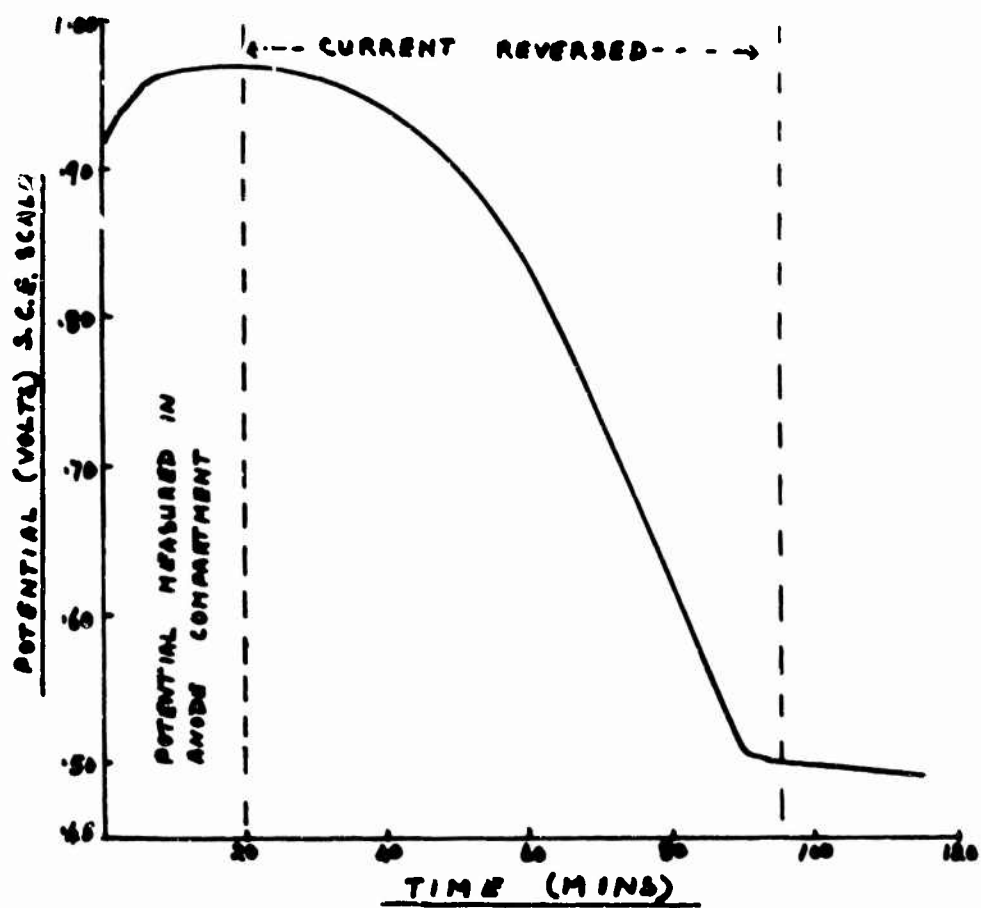


Fig. 33 Application of potentials via carbon electrodes to the ferrous-ceric system.

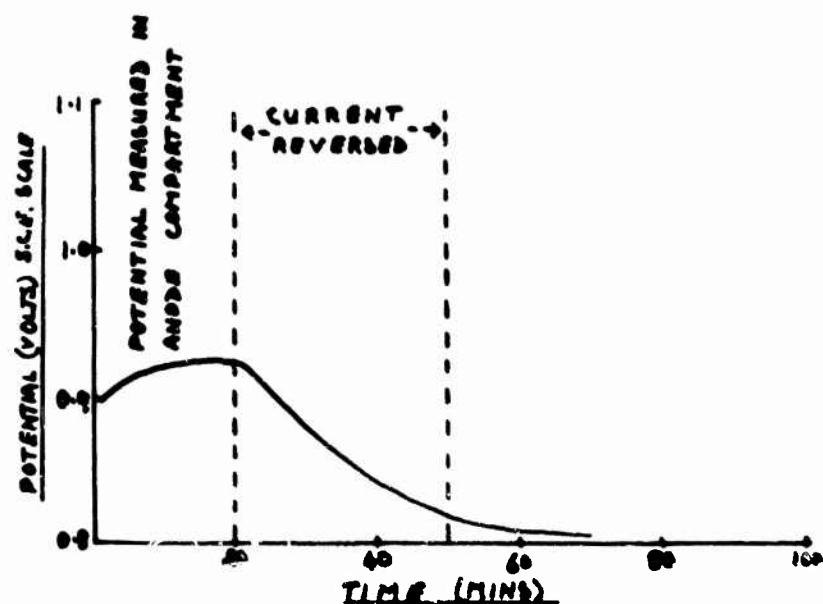


Fig. 34 Application of potentials via mercury electrodes to the ferrous-ceric system.

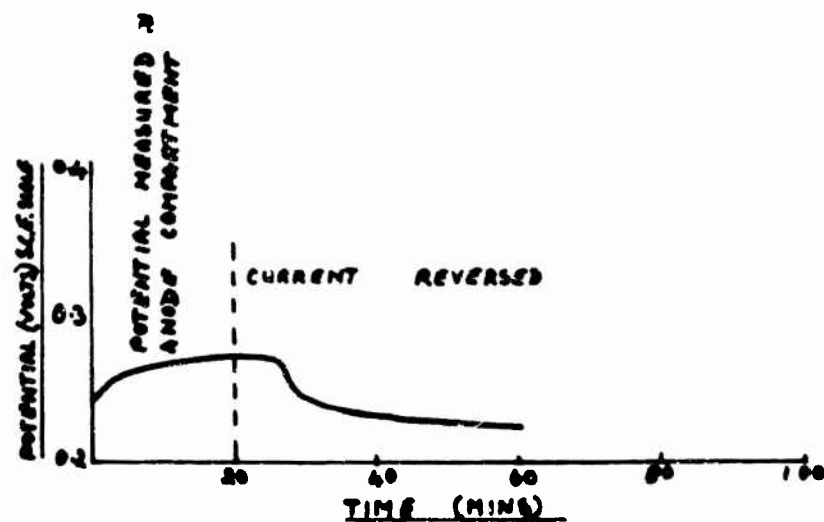


Fig. 35 Application of potentials via copper electrodes to the ferrous-ferric system.

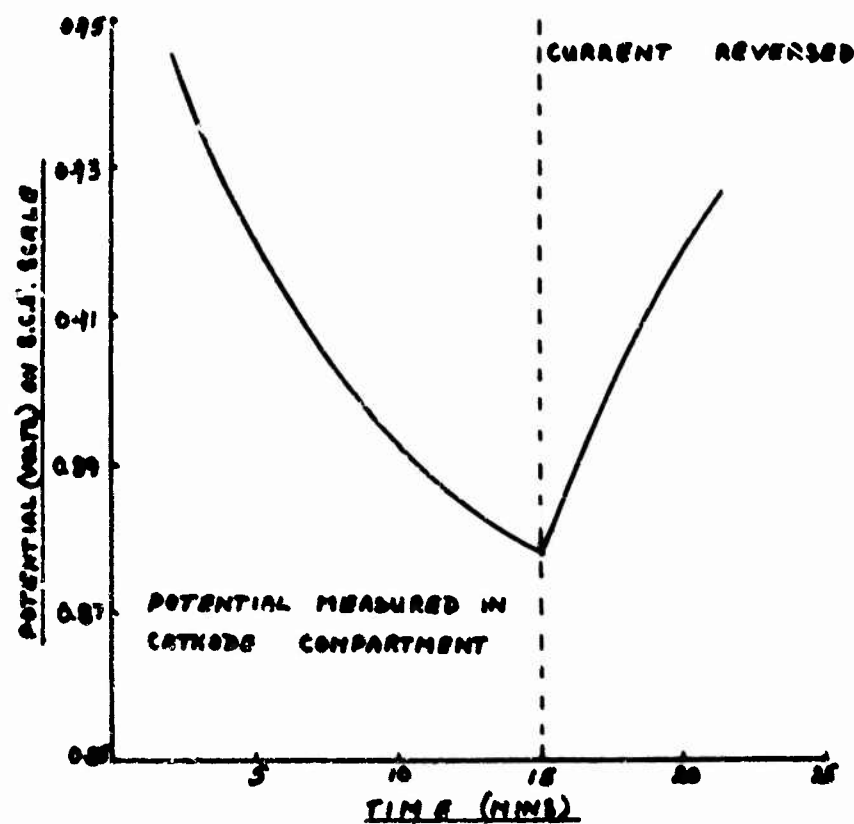


Fig. 36 Application of potentials to the ferrous-ceric system in 0.5N acid.
A copper cathode and a gold anode.

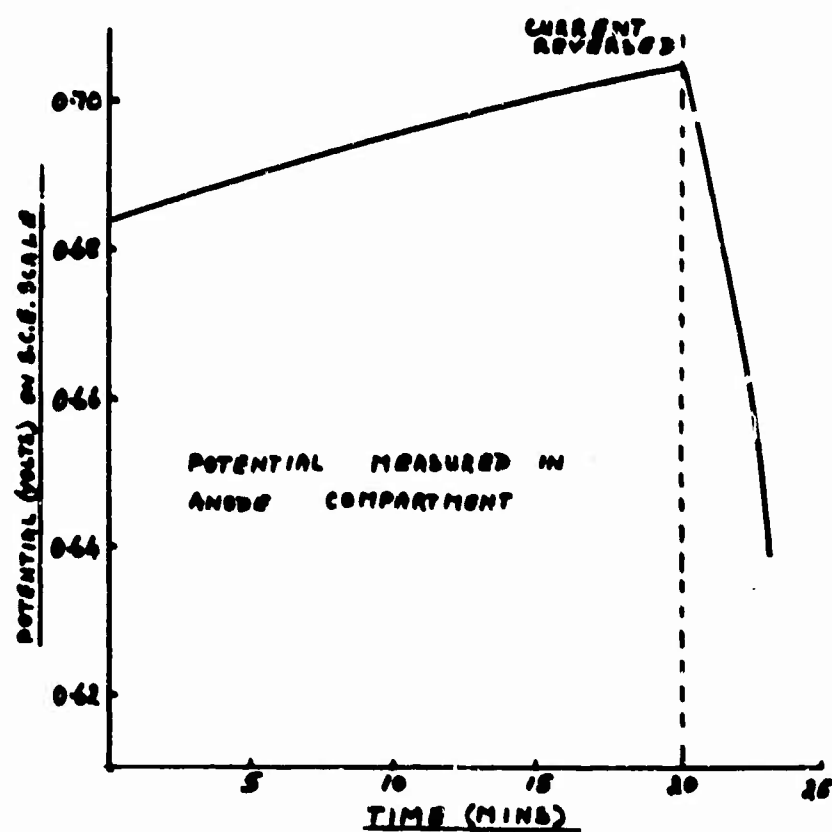


Fig. 37 Application of potentials to the ferrous-ceric system in 4.8M acid. A copper cathode and a gold anode.

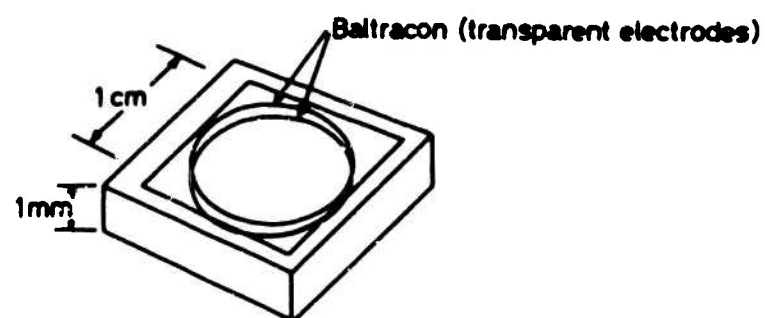


Fig.38 Early cell with tin oxide transparent electrodes

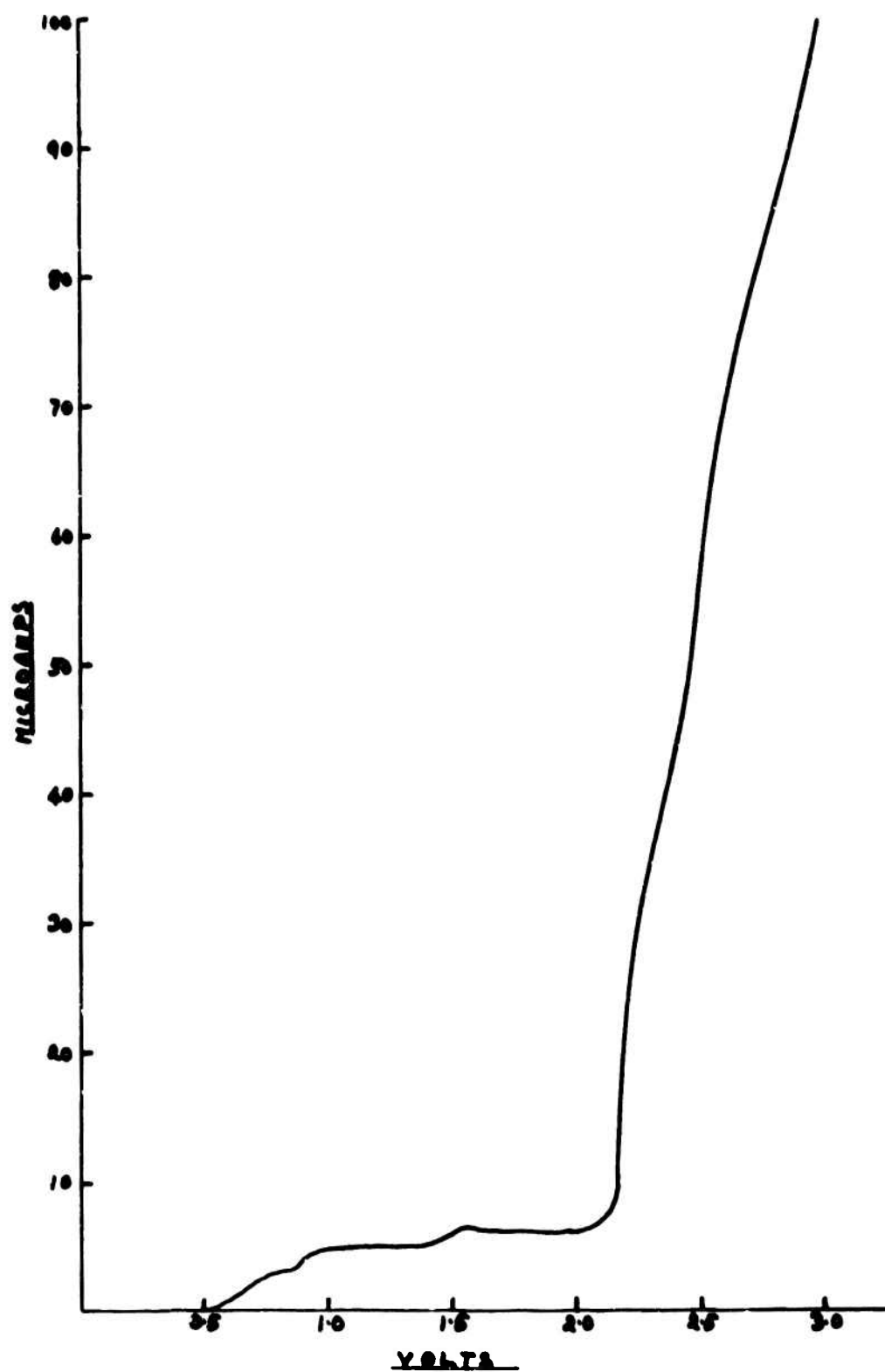


Fig. 39 Polarogram of benzyl viologen dichloride.

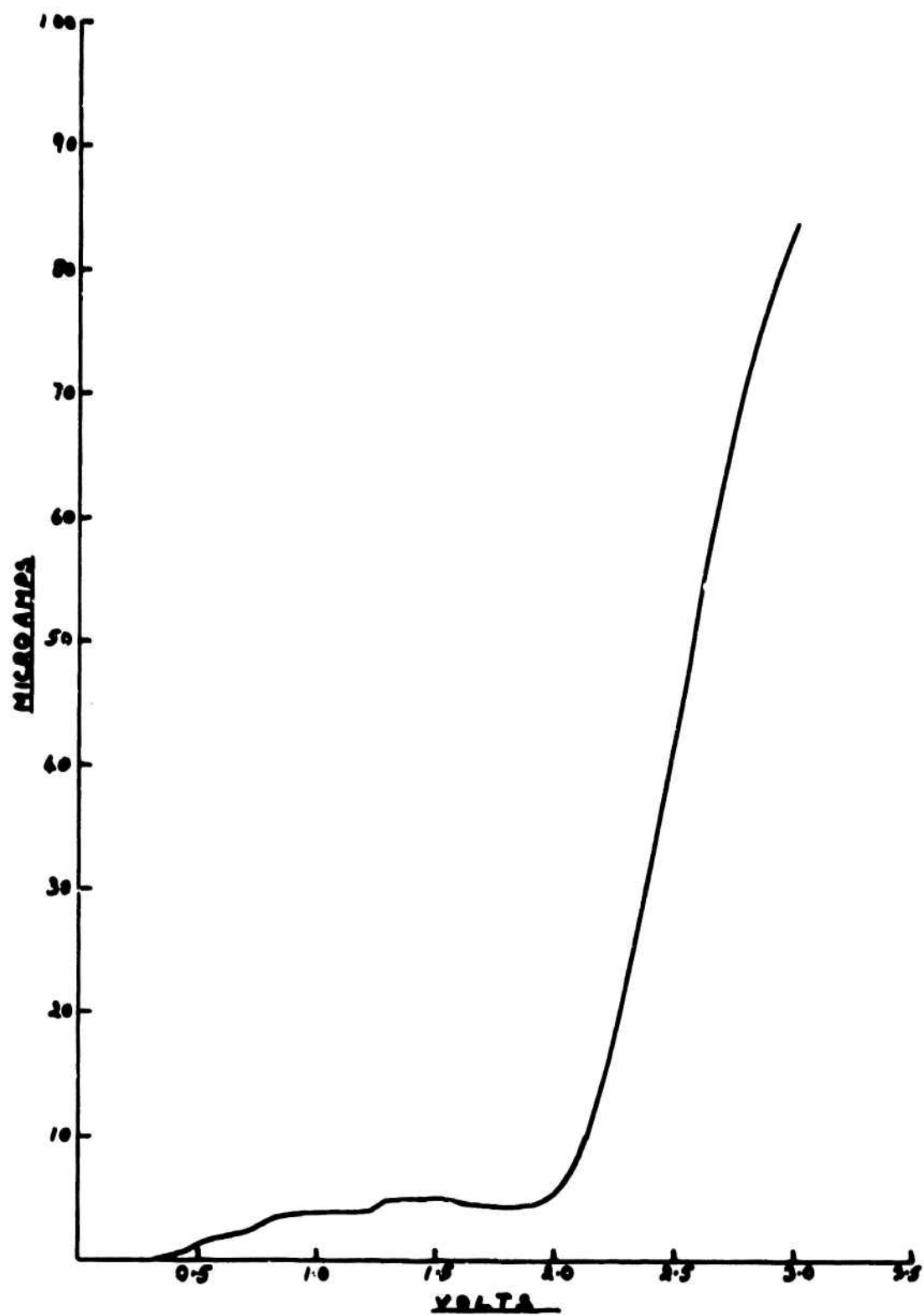


Fig. 40 Polarogram of heptyl viologen dibromide.

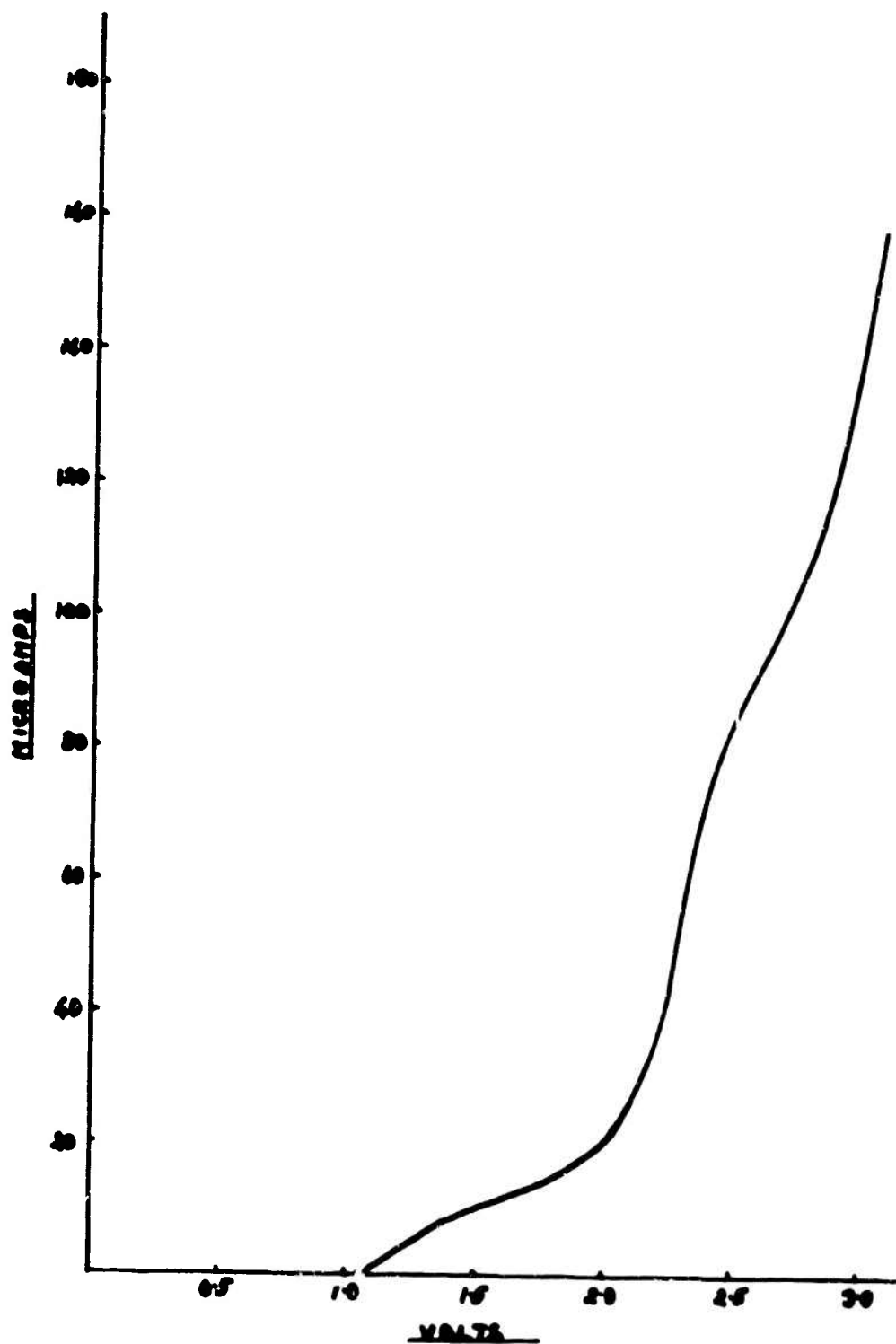


Fig. 41 Voltage-current relationship for heptyl viologen dibromide.

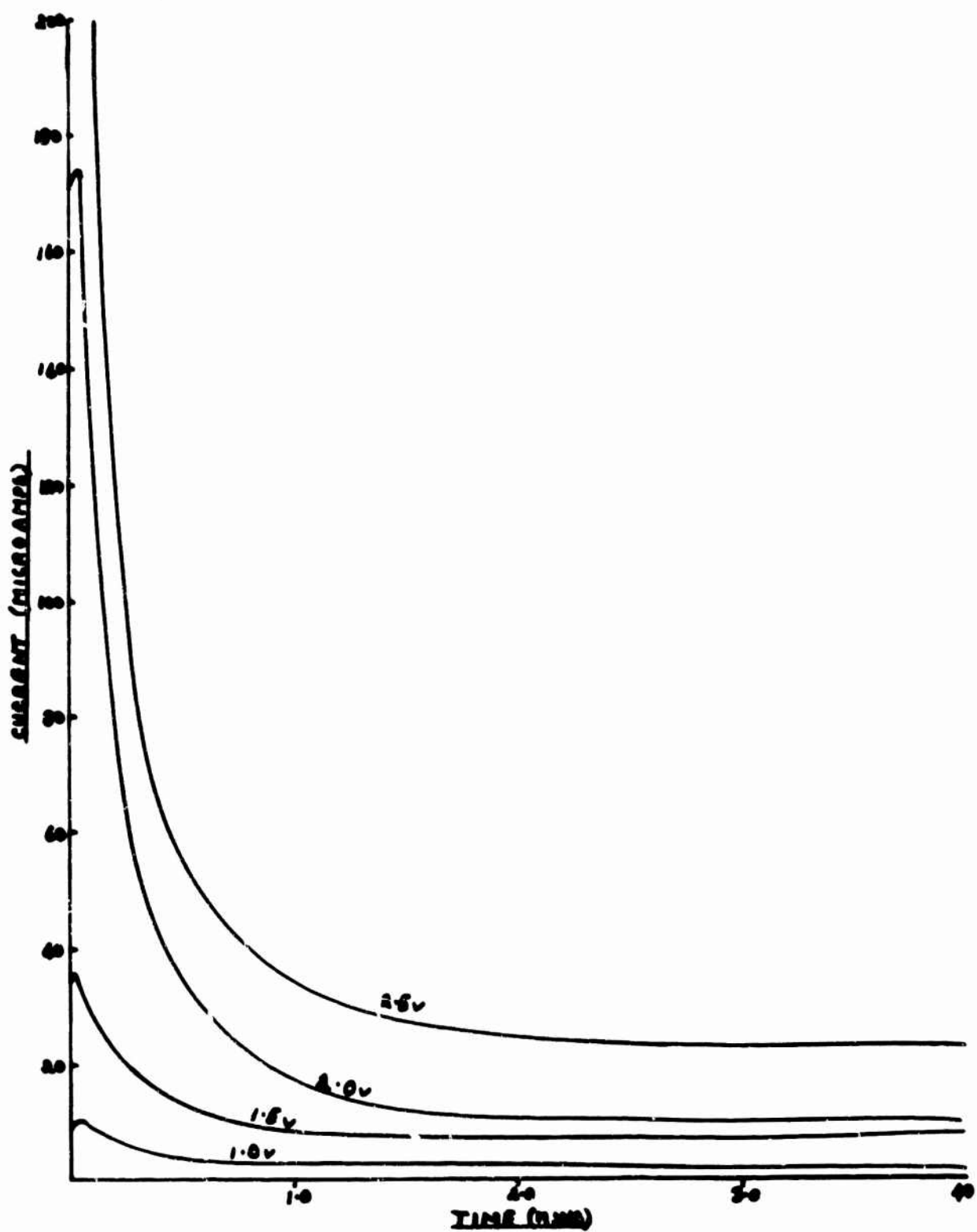
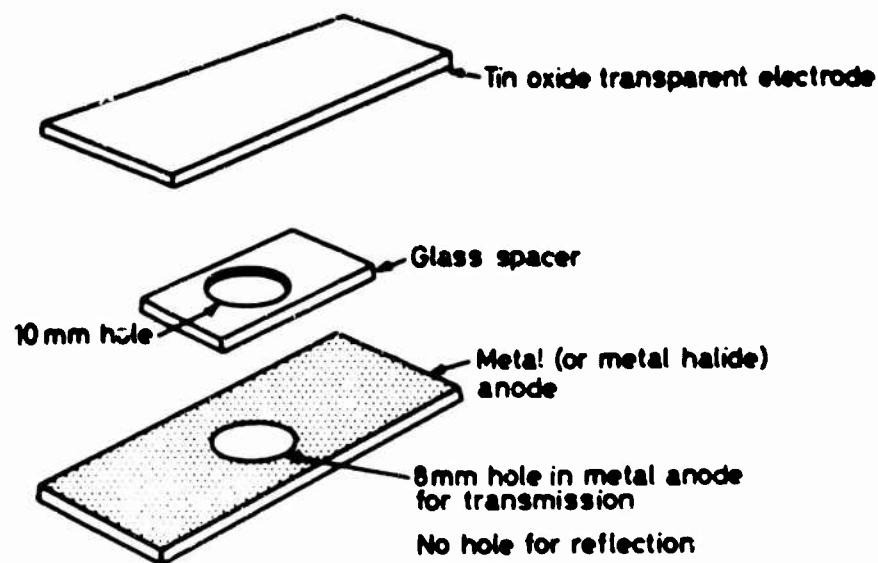
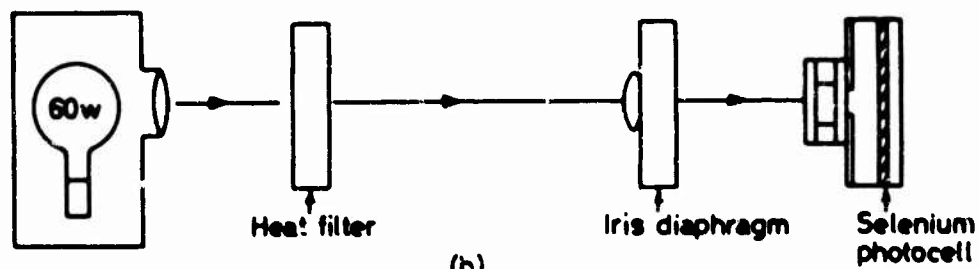


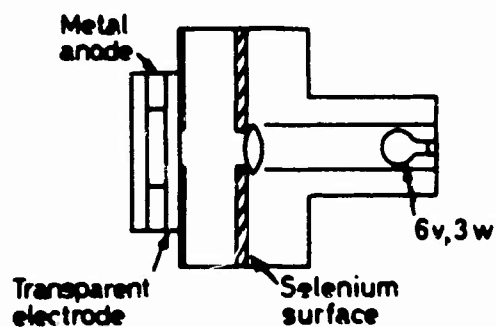
Fig. 42 Current-time curves at constant voltages for heptyl viologen dibromide.



(a)



(b)



(c)

Fig.43 (a) Cell design for light measurement experiments
 (b) Apparatus for light transmission measurements
 (c) Apparatus for light reflectance measurements

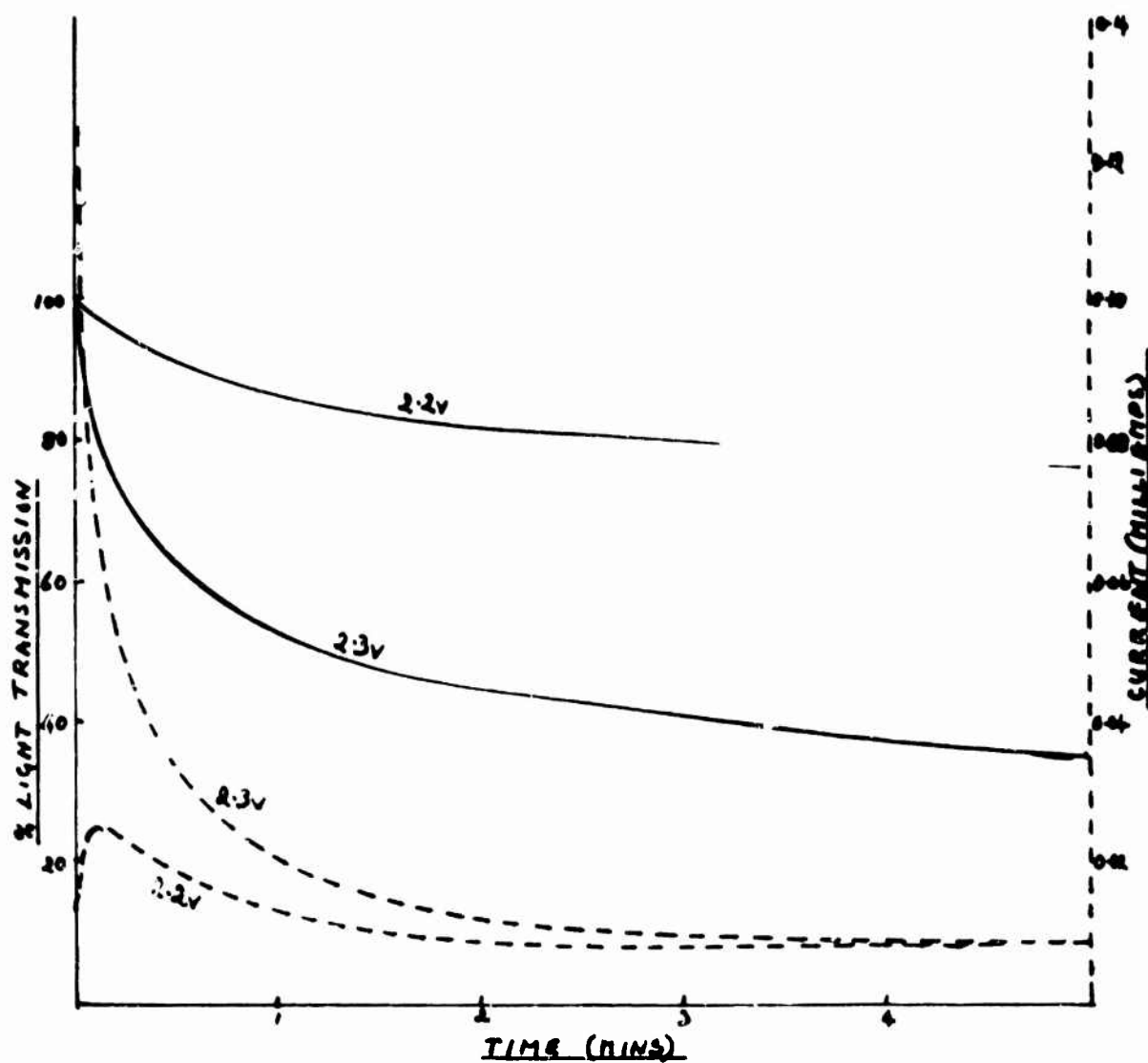


Fig. 44 Light transmission, current versus time curves for compound (I). Two transparent tin oxide electrodes.

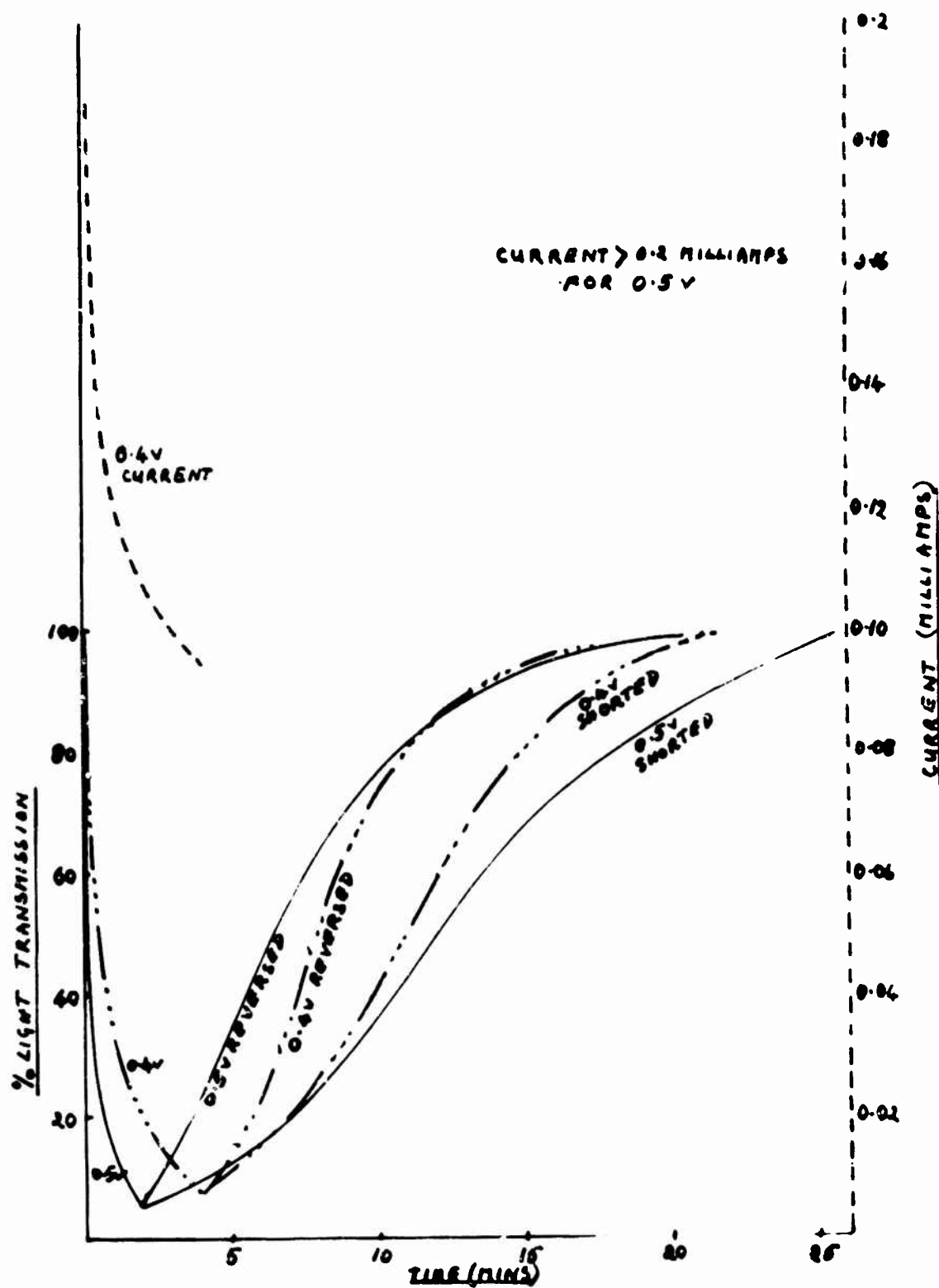


Fig. 45 Light transmission and current versus time curves for compound (I).
A tin oxide transparent cathode and a copper anode.

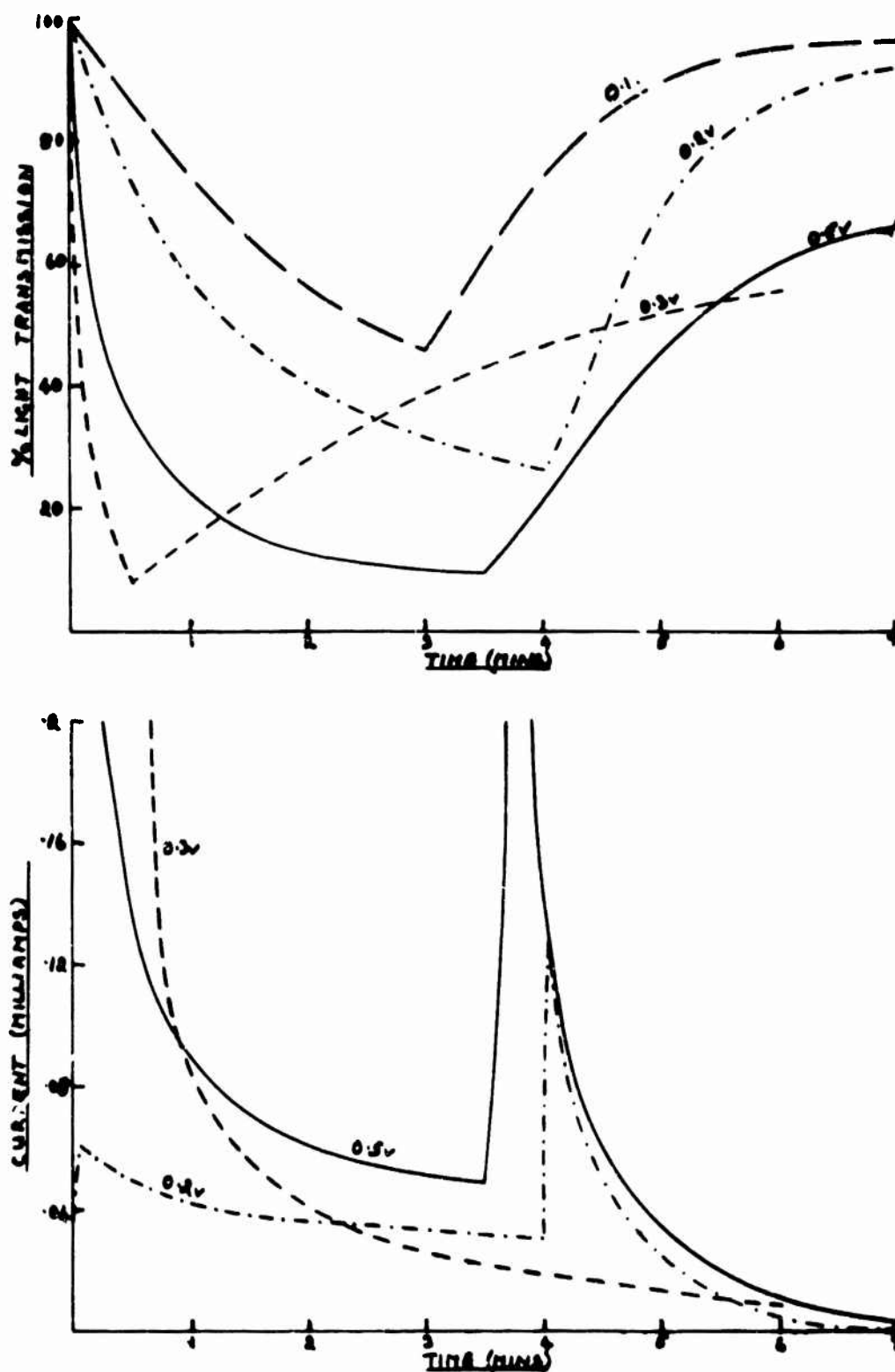


Fig. 46 Light transmission and current versus time curves for compound (I).
A tin oxide transparent cathode and a lead anode.

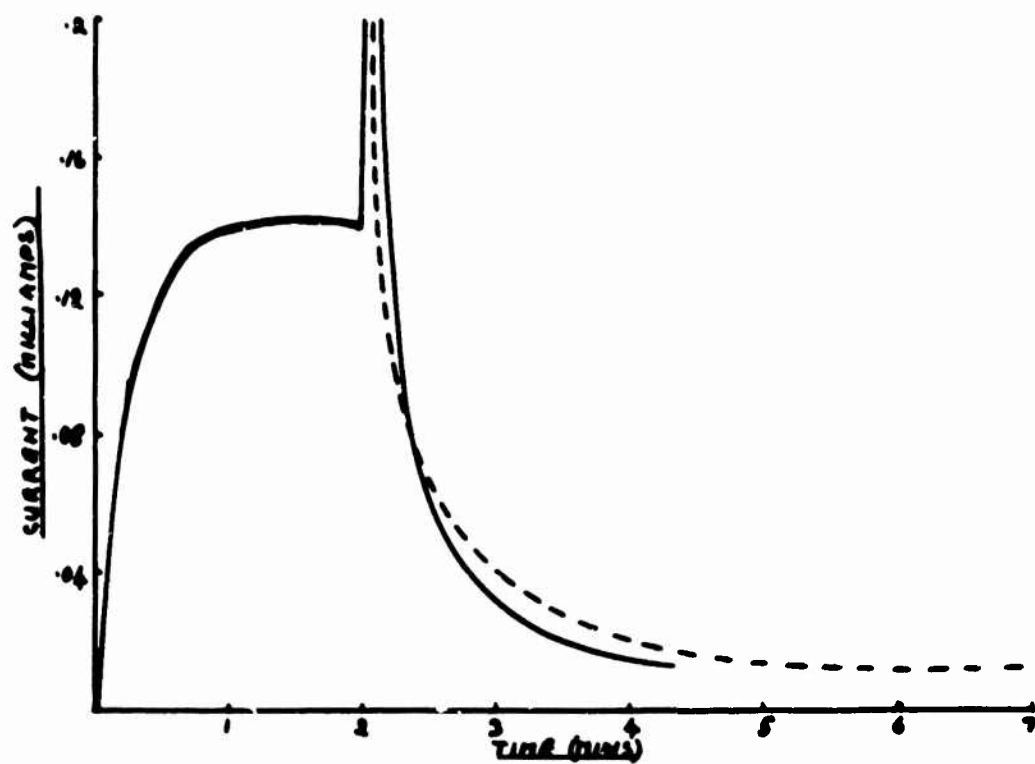
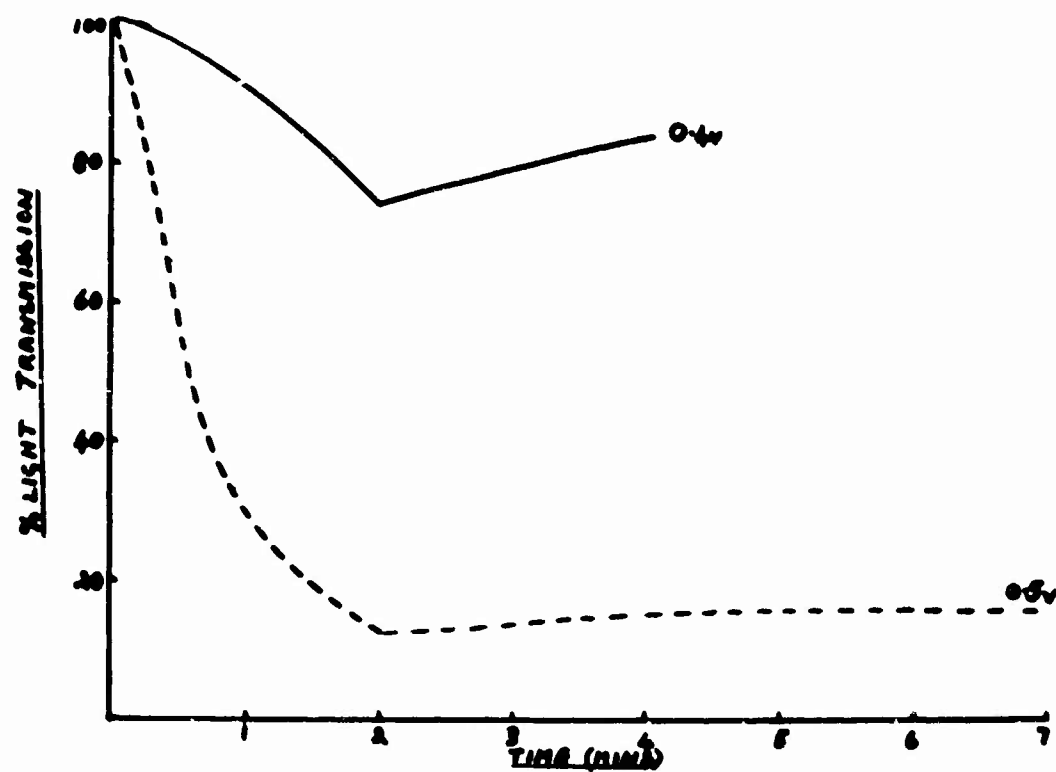


Fig. 47 Light transmission and current versus time curves for compound (I).
A tin oxide transparent cathode and a silver anode.

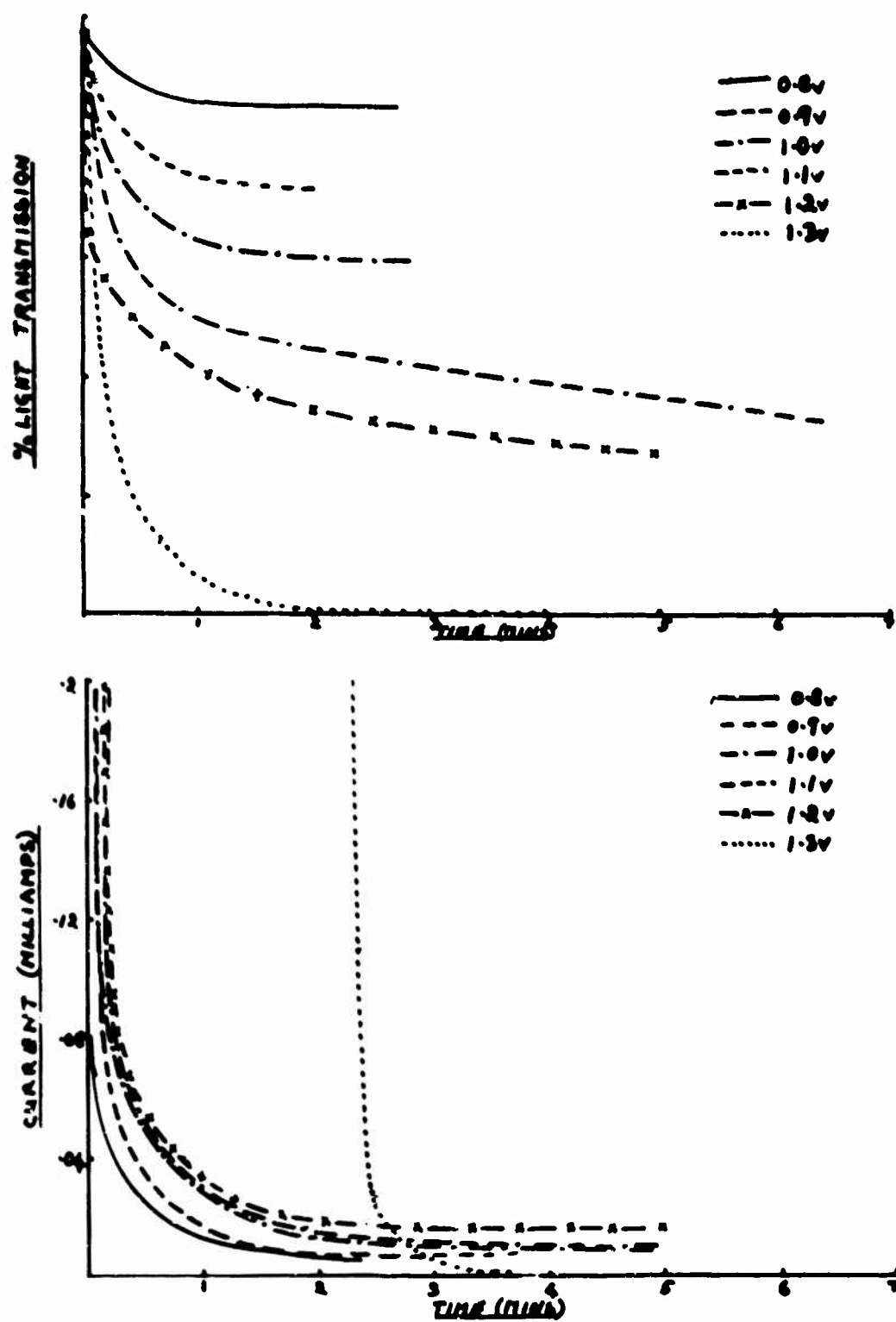
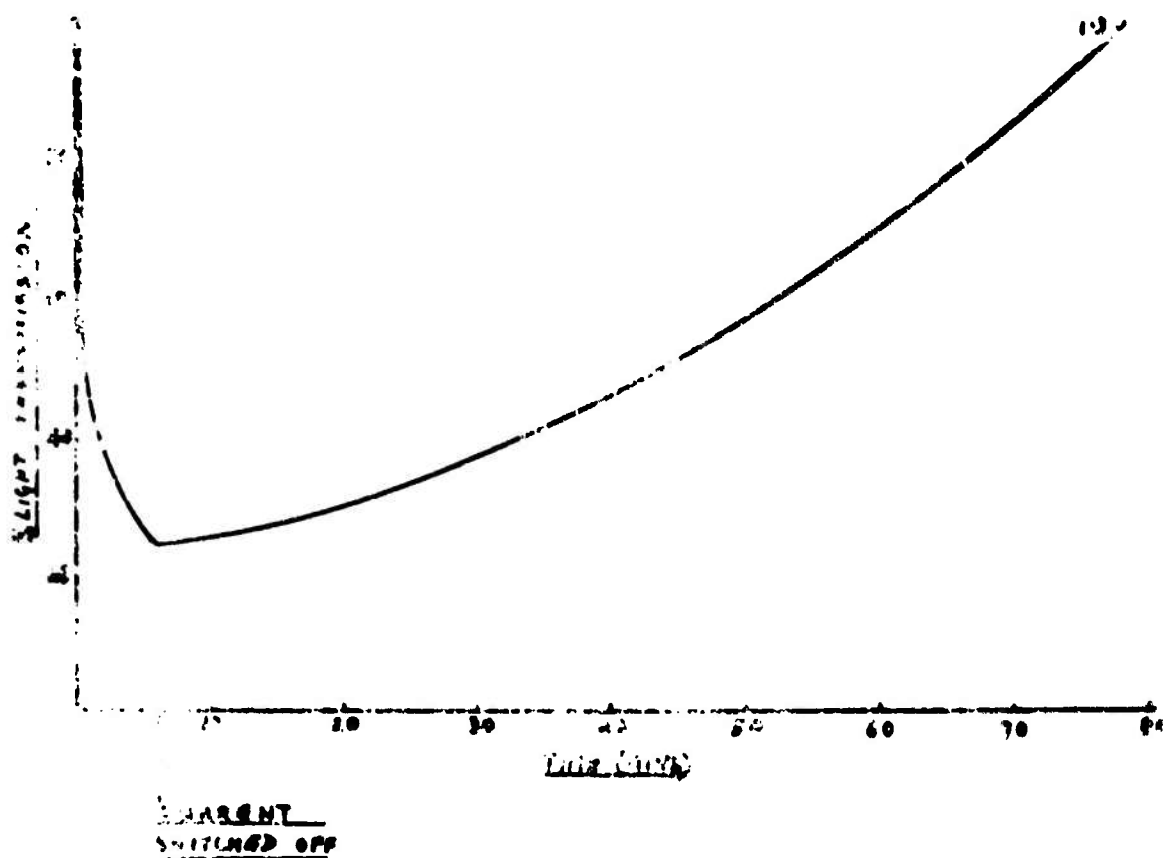


Fig. 48 Light transmission and current versus time curves for compound (I).
A tin oxide transparent cathode and a silver-silver bromide anode.

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transmission delay of the compound (1). A thin white translucent cathode and a silver-silver bromide anode.

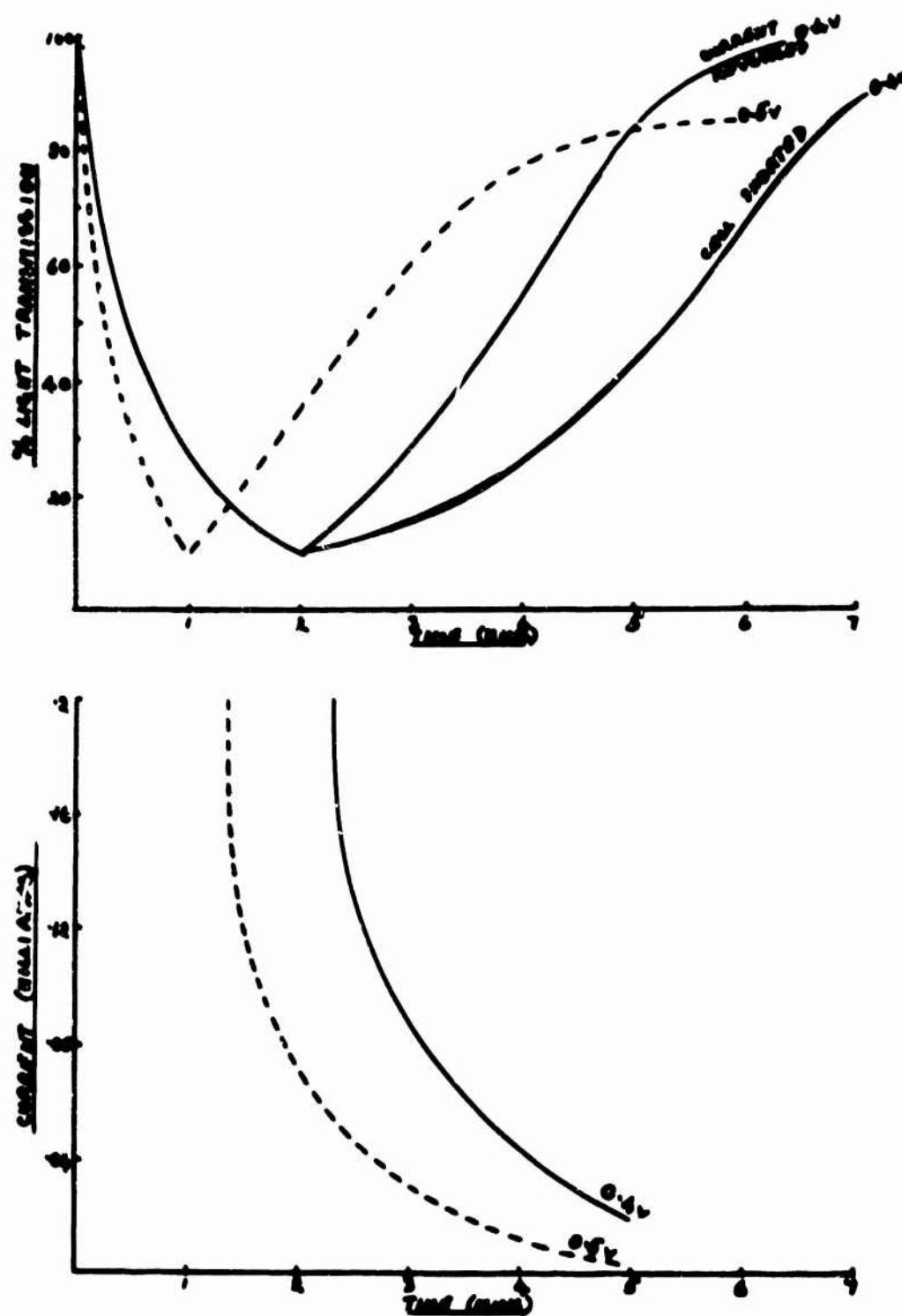


Fig. 50 Light transmission and current versus time curves for compound (I) with potassium bromide. A tin oxide transparent cathode and a silver-silver bromide anode.

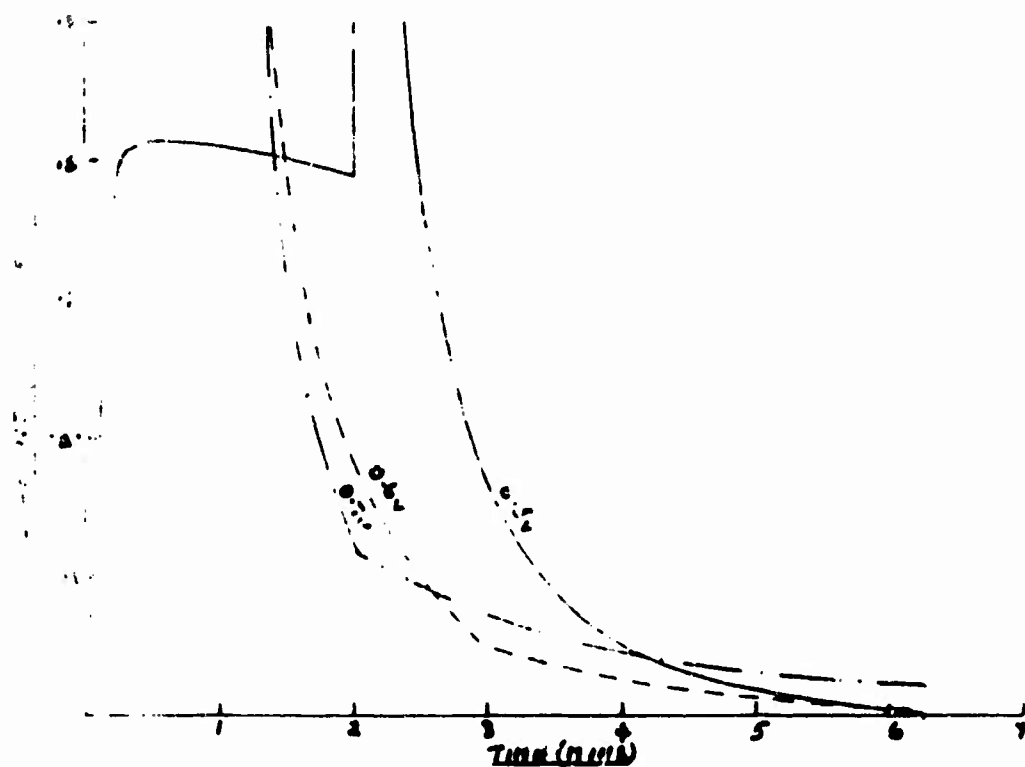
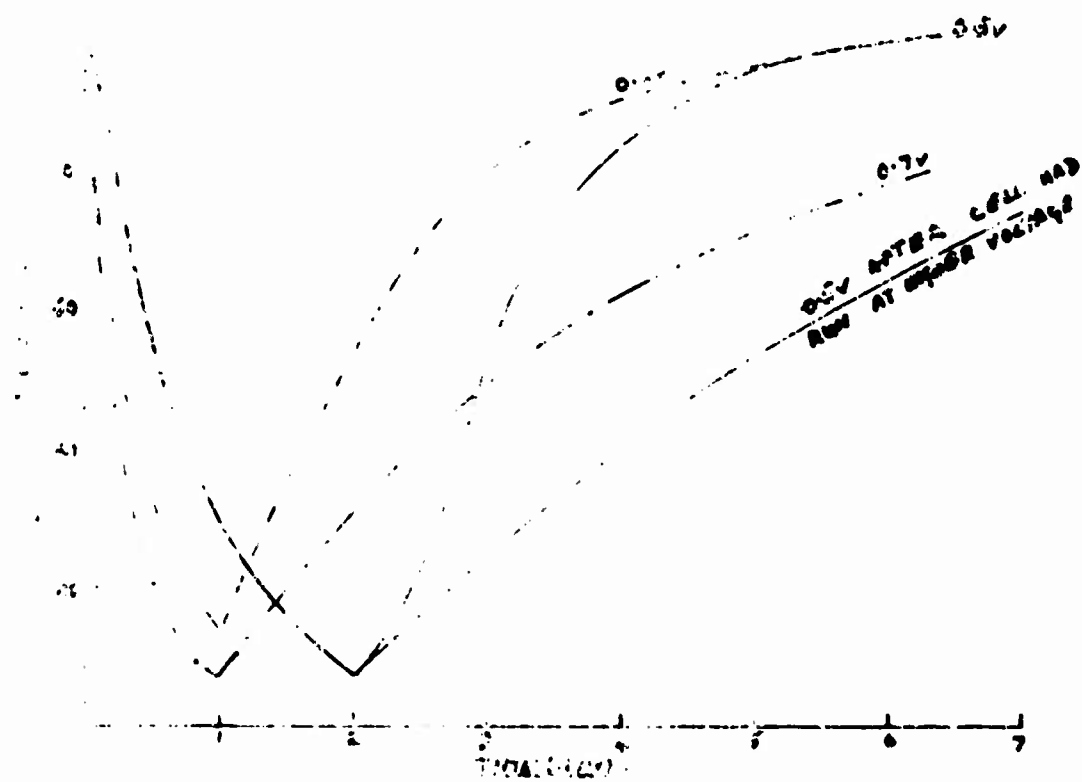


Fig. 7. Light transmission and current versus time curves for compound (I).
 A. 0.5V; B. 0.7V; C. 0.9V. Cell was at 0.5V for 10 min before 0.9V was applied.

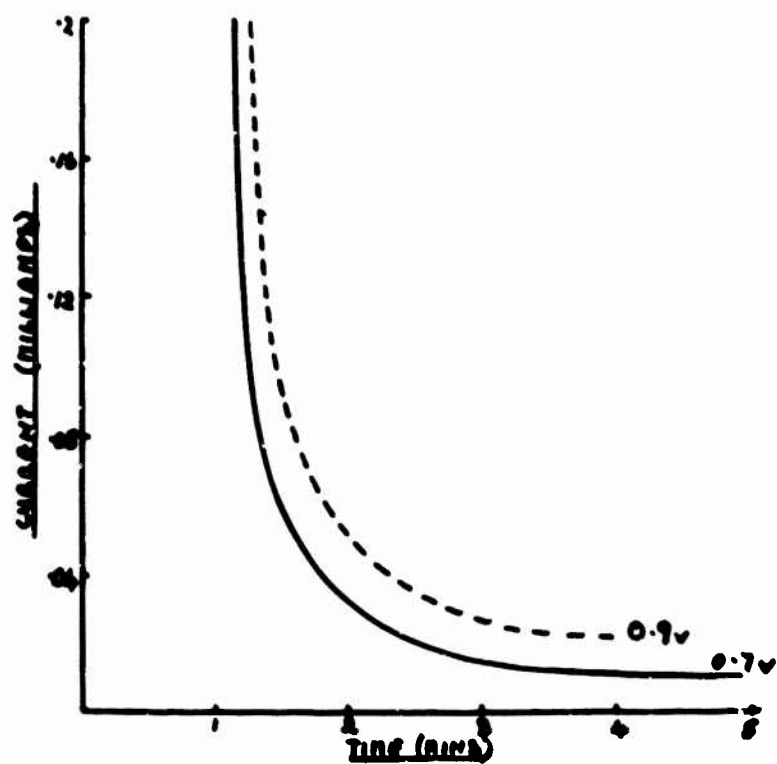
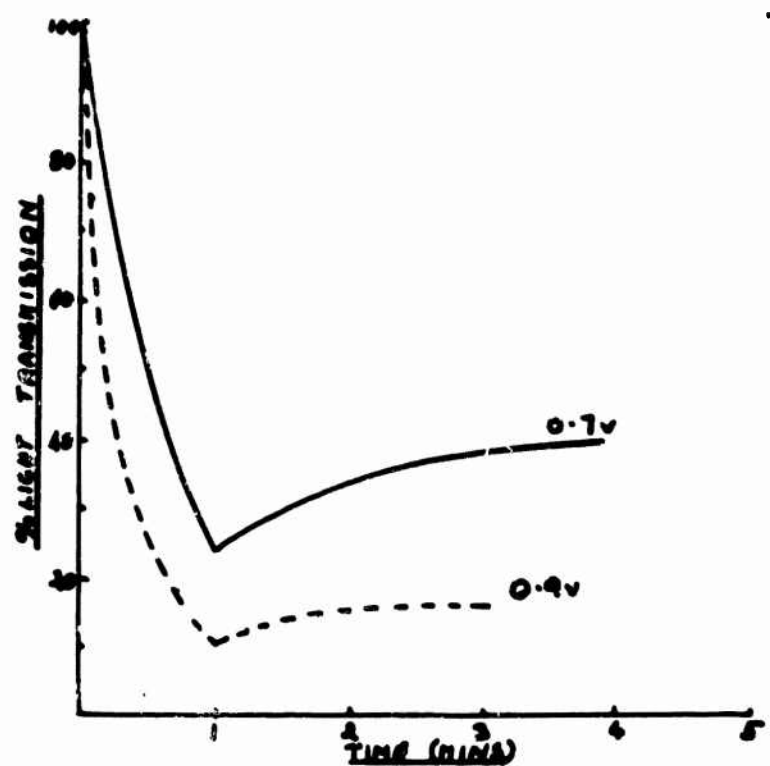


Fig. 52 Light transmission and current versus time curves for compound (I) with ferrous ammonium sulphate. A tin oxide transparent cathode and a silver-silver sulphate anode.

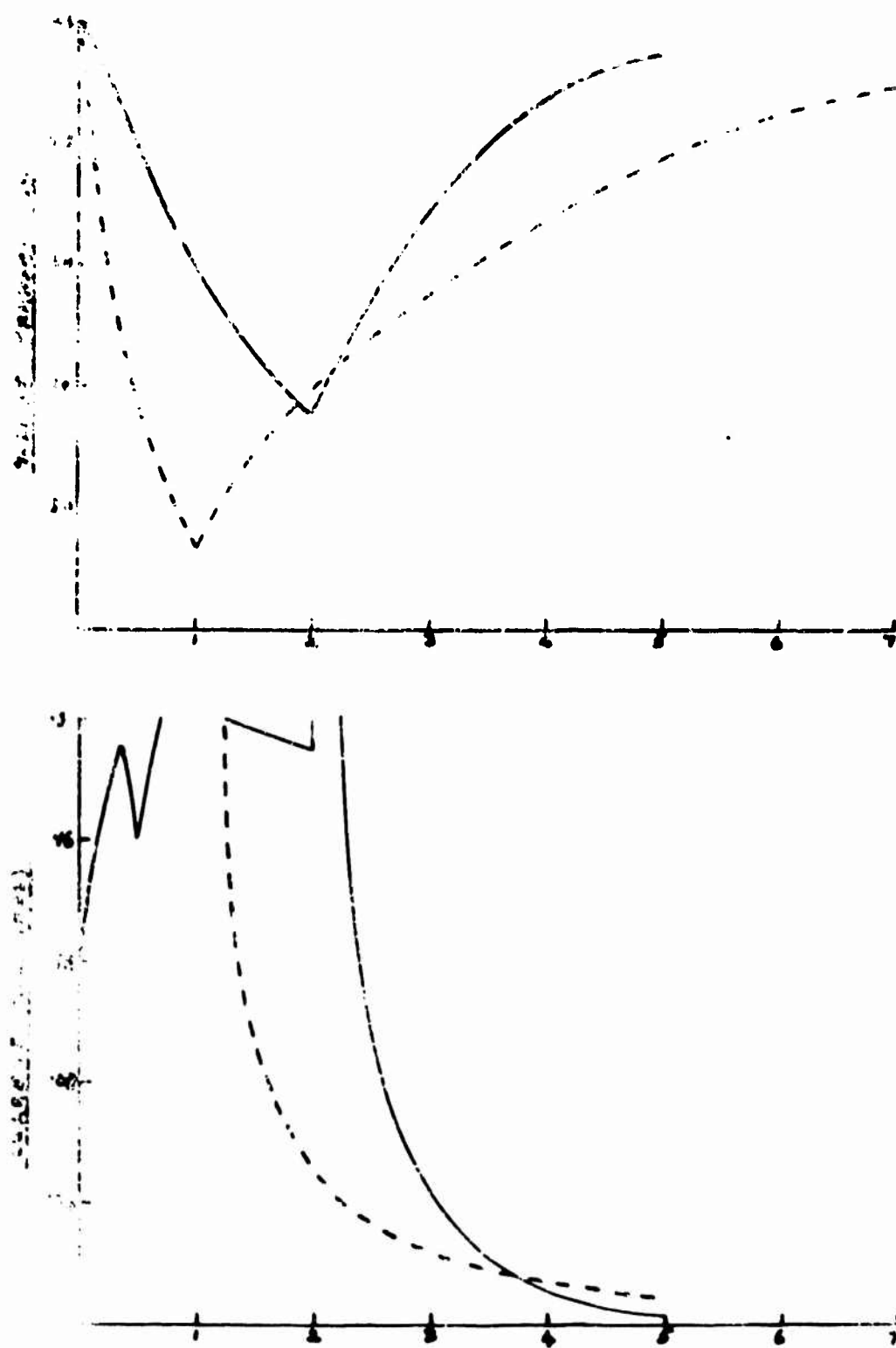


Fig. 53 Light transmission and current versus time curves for compound (I).
A tin oxide transparent cathode and a silver-silver molybdate anode.

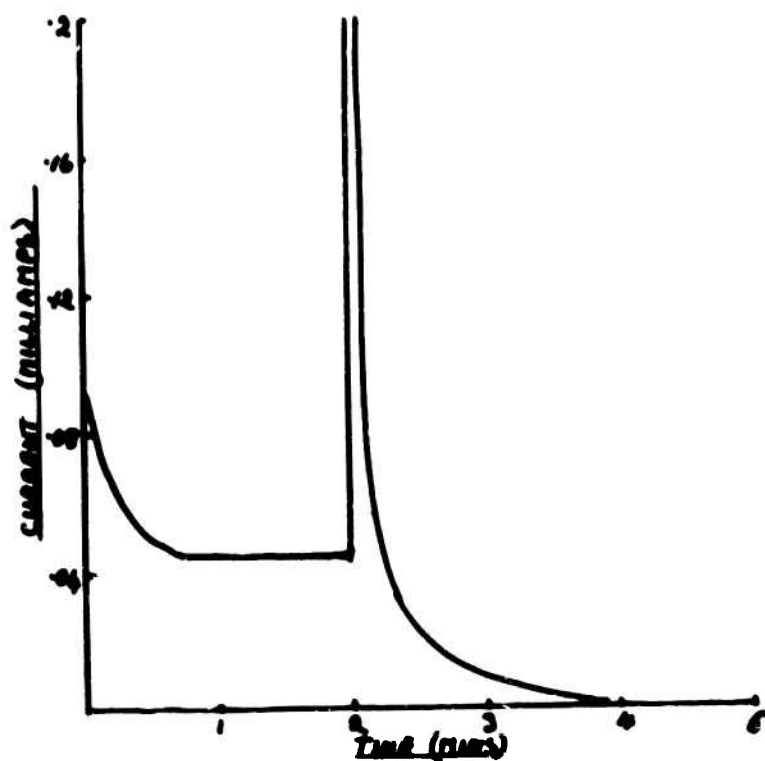
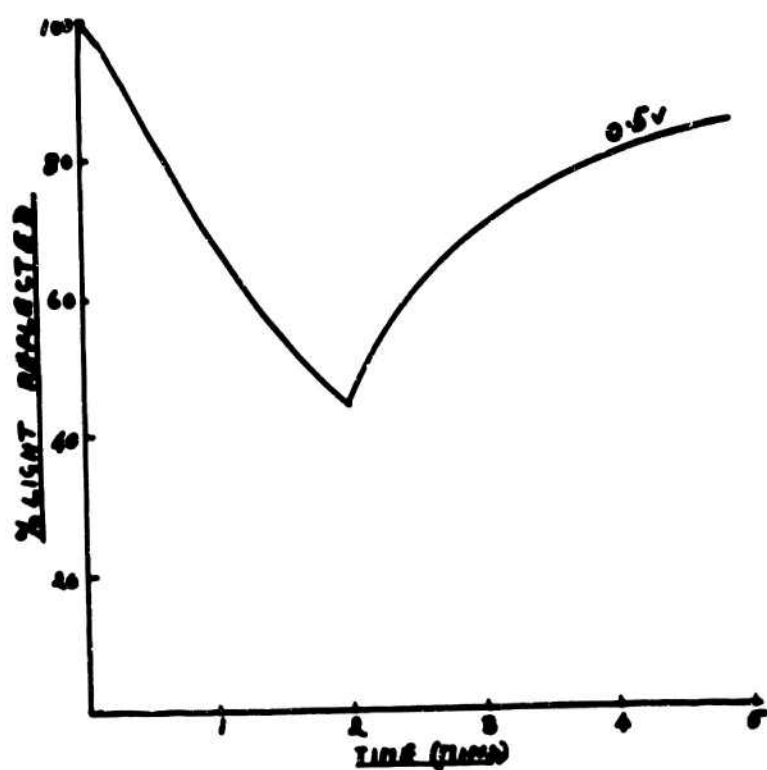


Fig. 54 Light reflected and current versus time curves for compound (I).
A tin oxide transparent cathode and a silver anode.

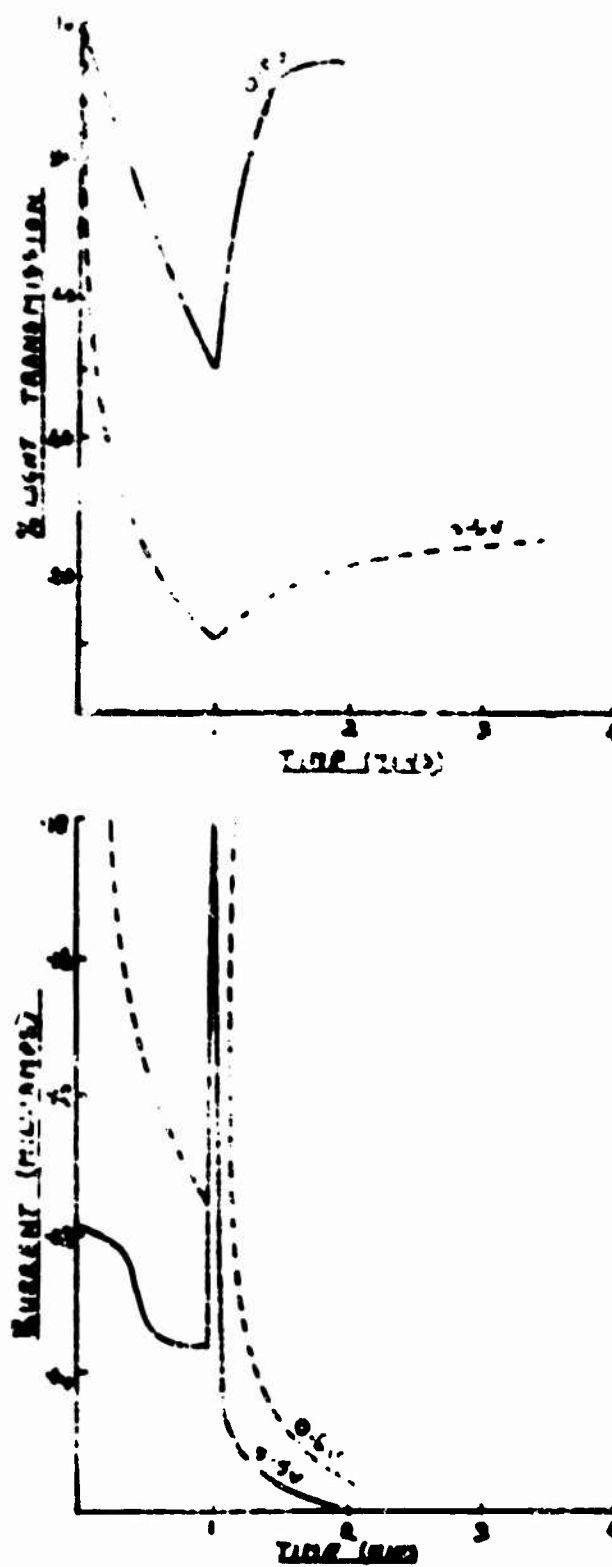


Fig. 55 Light transmission and current versus time curves for compound (I).
A tin oxide thin film deposited on a silver oxide

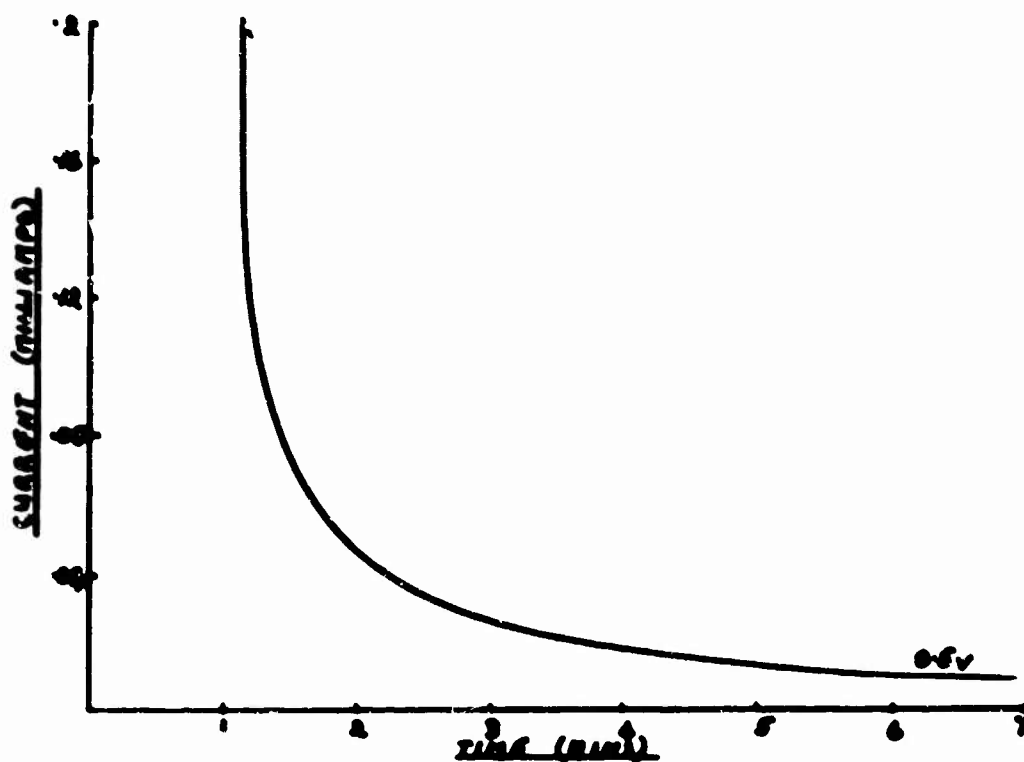
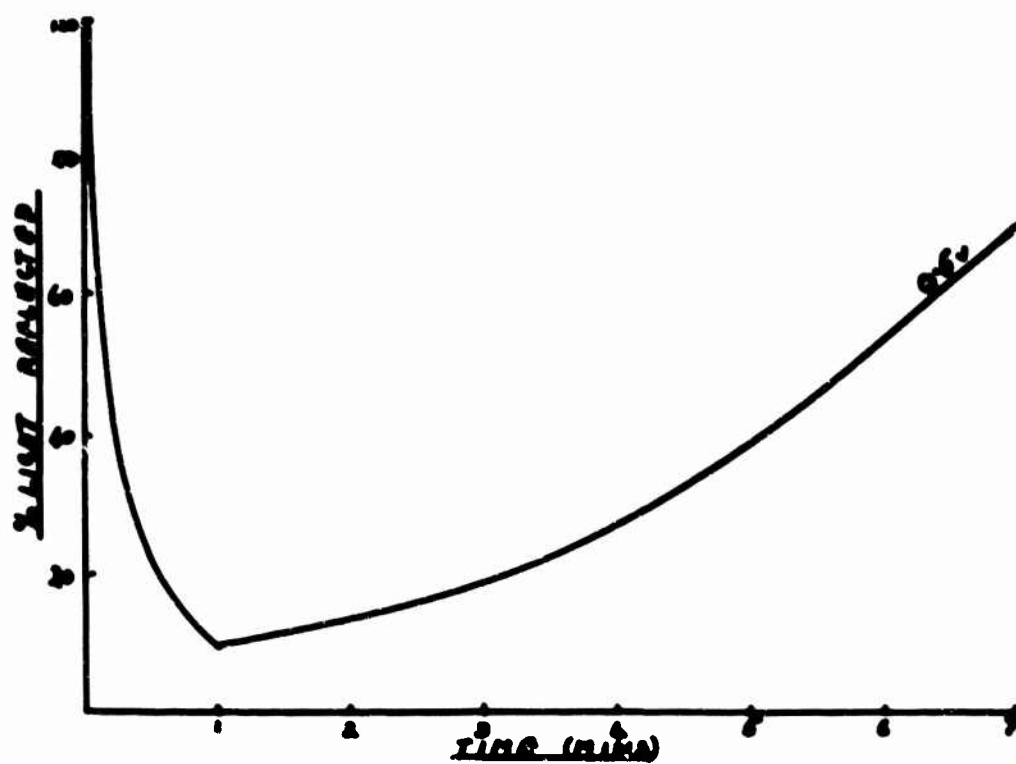


Fig. 56 Light reflected and current versus time curves for compound (I) with hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.

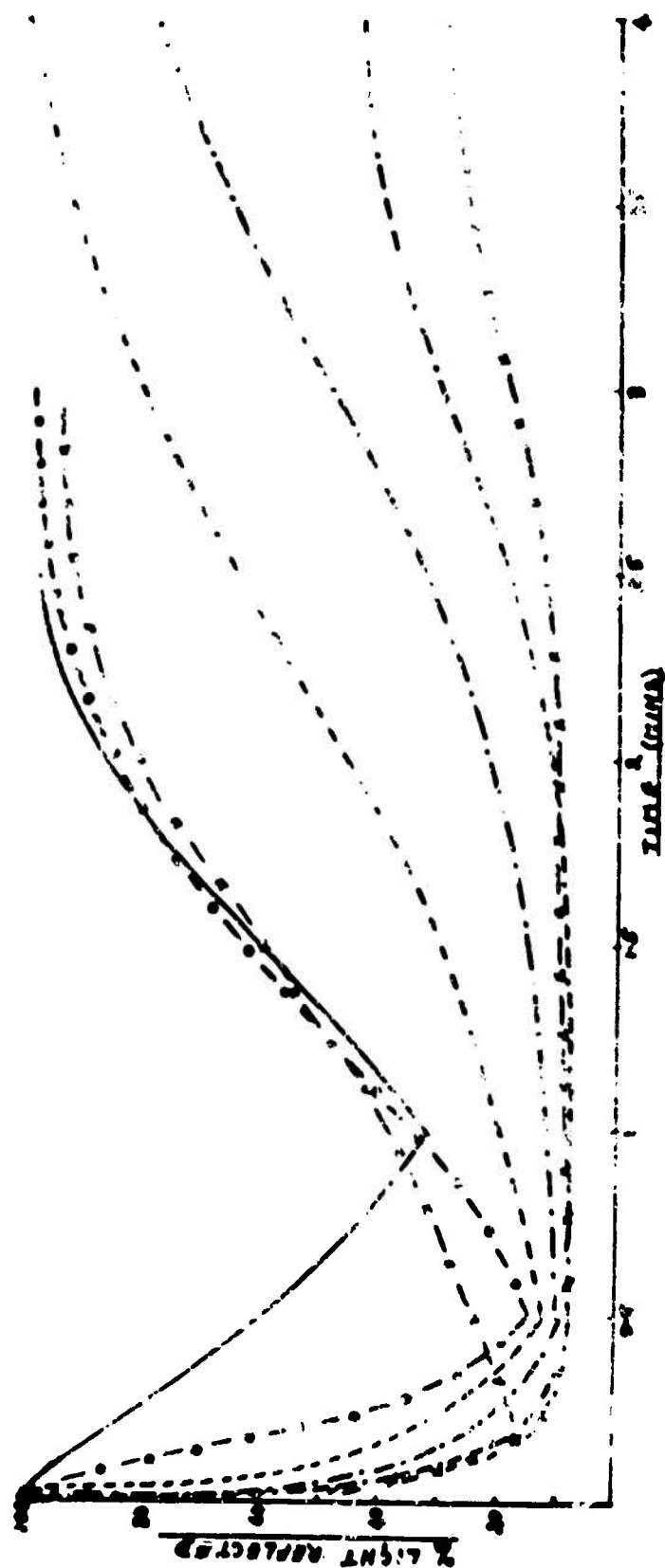


Fig. 57 Light absorbance versus time curves for compound (I) with hydroquinone (0.025M). A tin anode; transparent cathode and a silver anode.

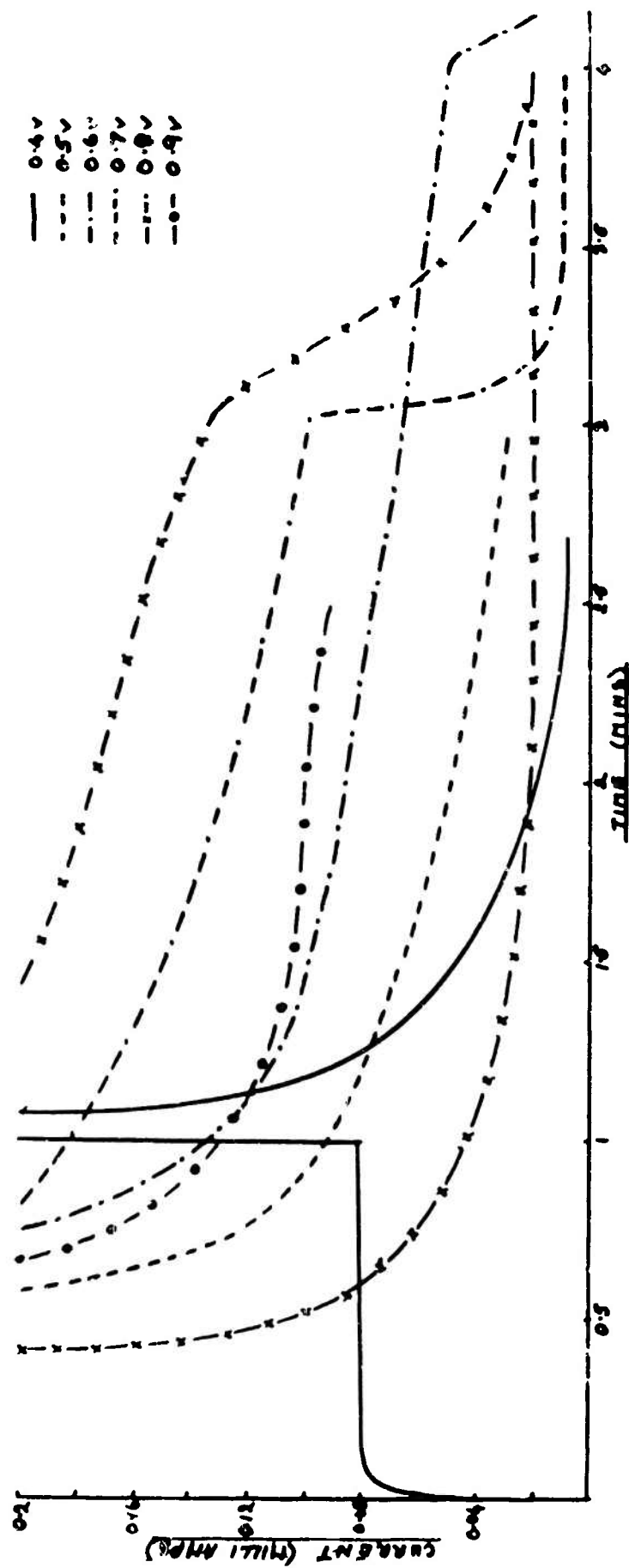


Fig. 58 Current versus time curves for compound (I) with hydroquinone (0.025M). A tin oxide transparent cathode and a silver anode.

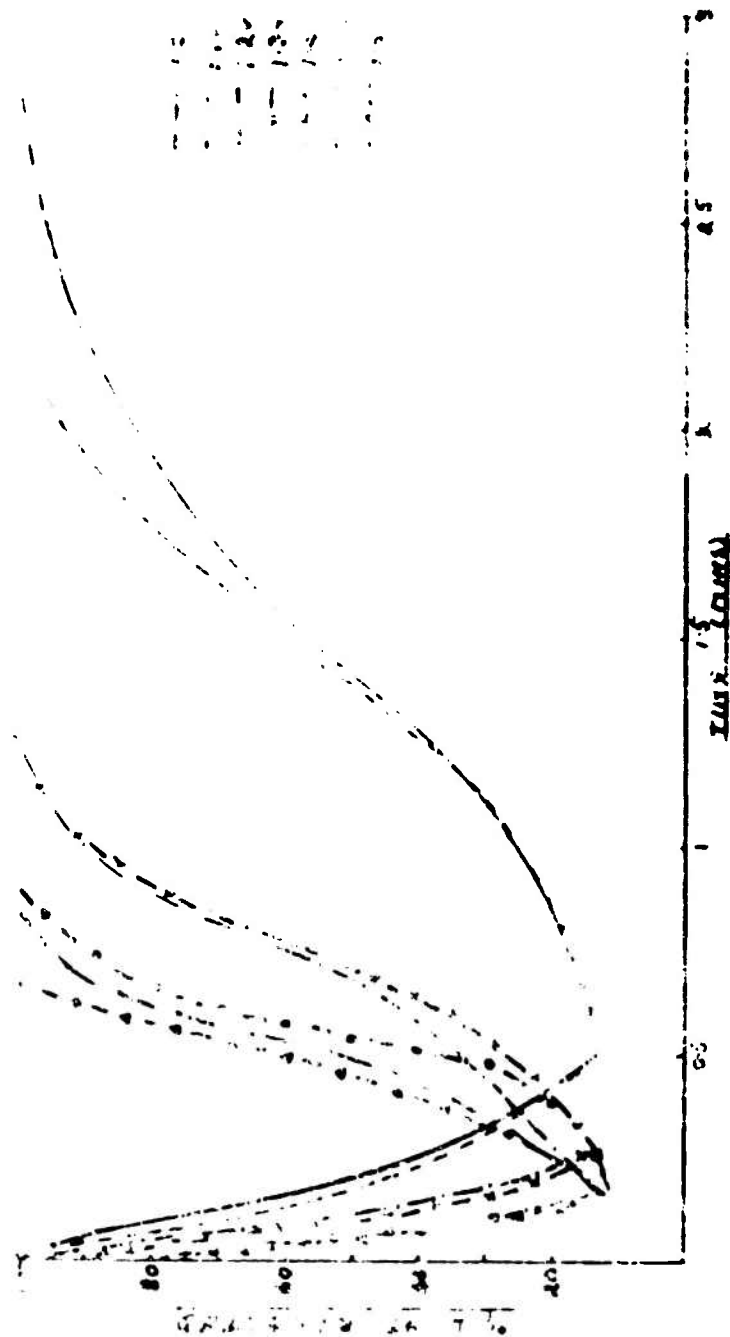


Fig. 1. Light intensity vs. time curves for cathode and anode. (1) Cathode, (2) Anode, (3) Cathode, (4) Anode, (5) Cathode, (6) Anode, (7) Cathode, (8) Anode, (9) Cathode, (10) Anode.

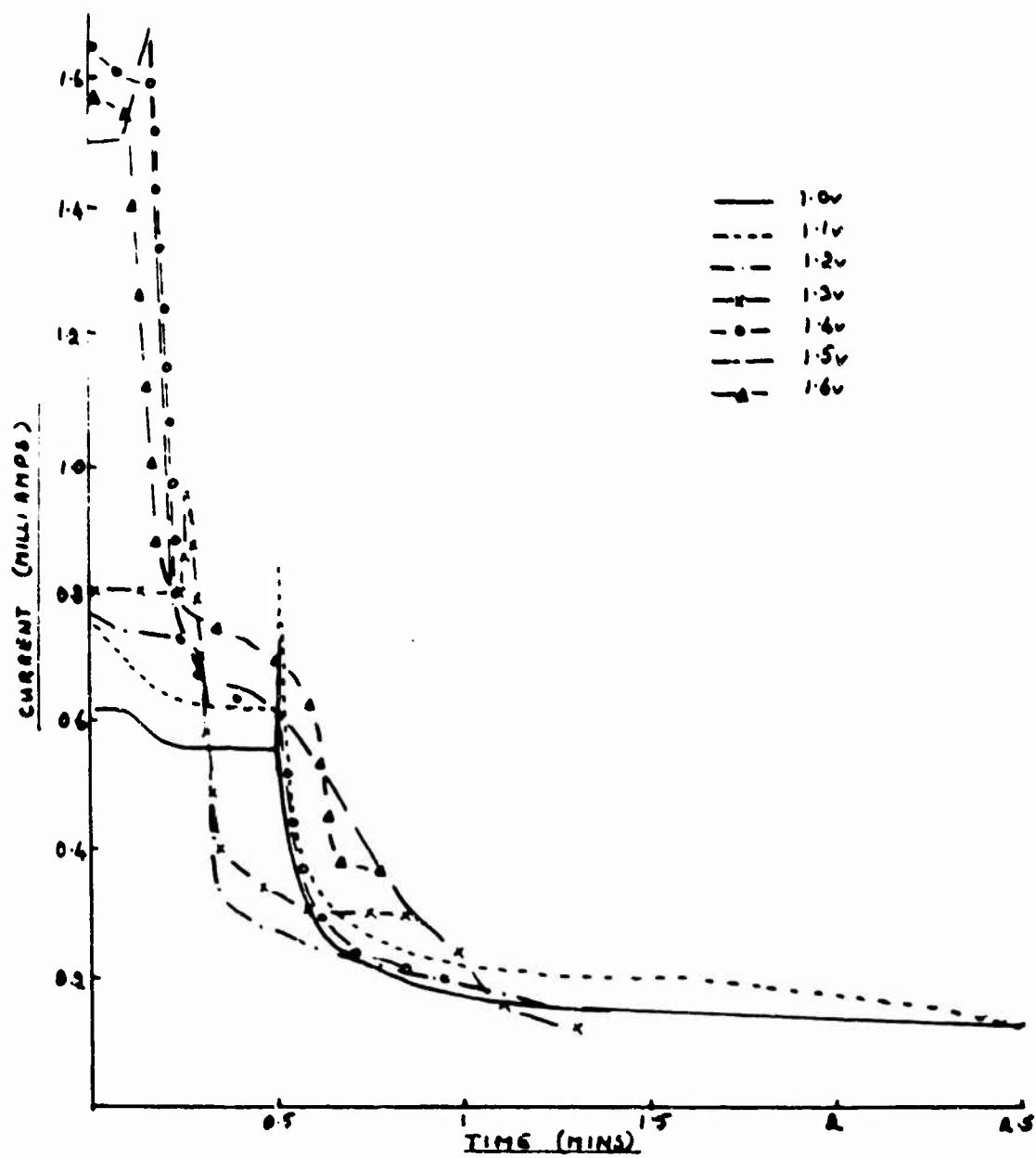


Fig. 60 Current versus time curves for compound (I) with hydroquinone (0.025M) continued. A tin oxide transparent cathode and a silver anode.

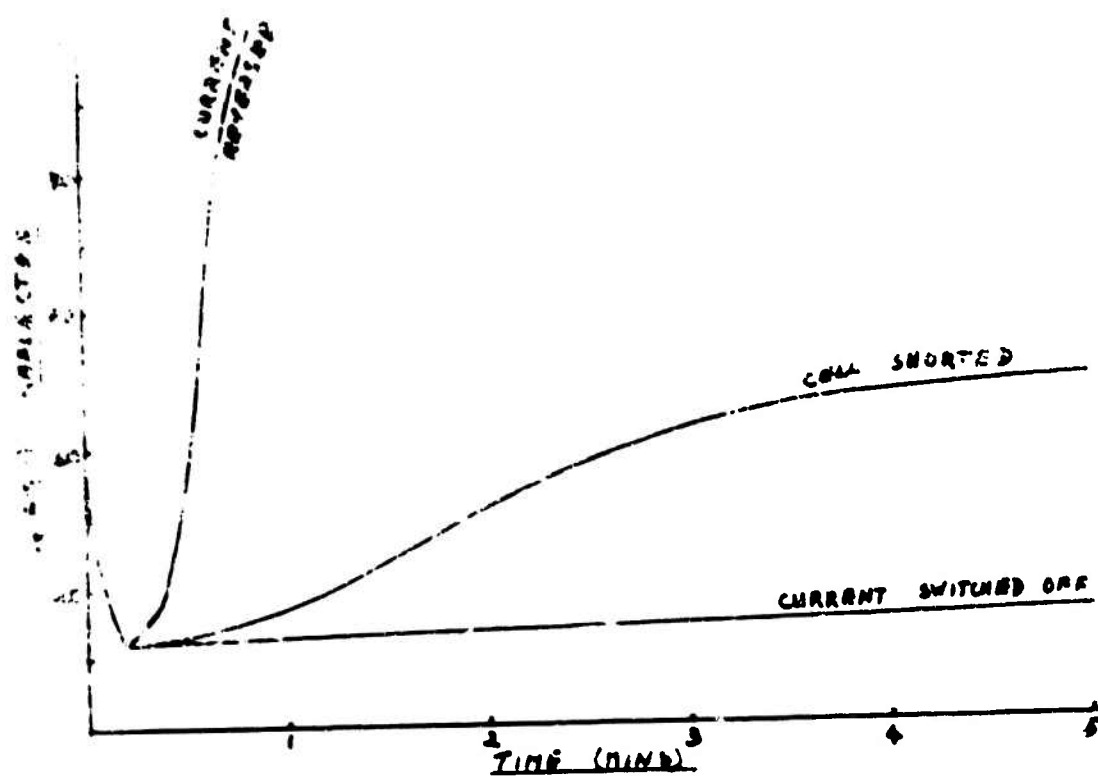


Fig. 10. Comparison of light reflected decay curves for compound (I) with p-benzoquinone (0.025M). A film of an transparent cathode and a silver anode.

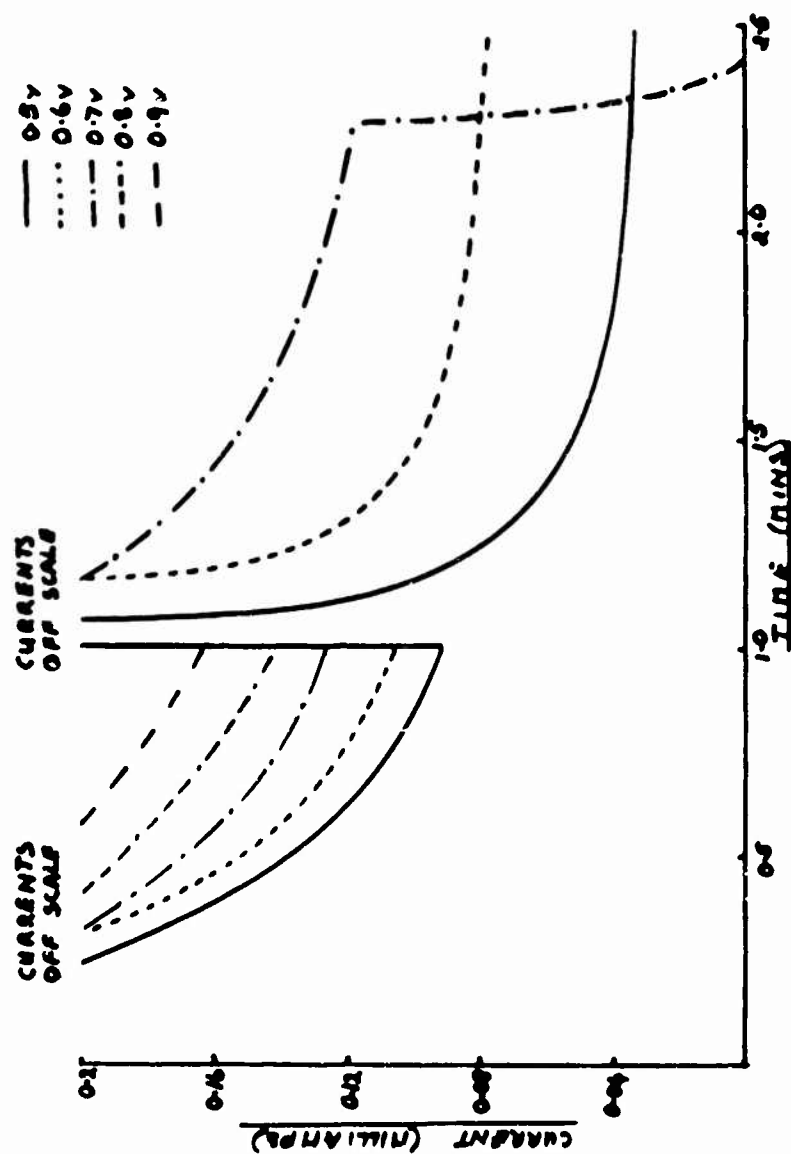
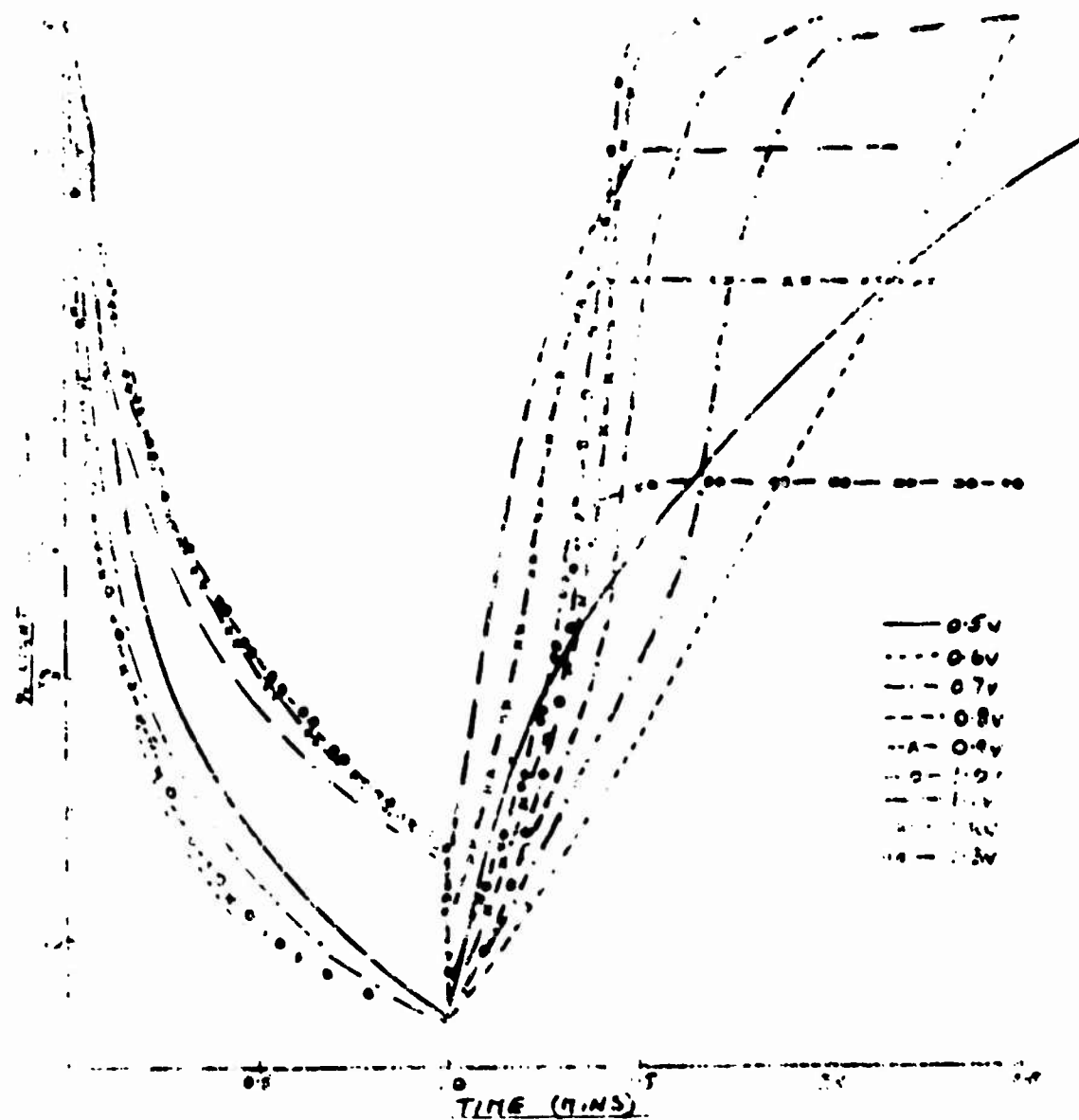


Fig. 62 Current versus time curves for compound (I) (2%) with supporting electrolyte and hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.



Light reflected versus time curves for compound (1) (2) with potassium bromide and hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.

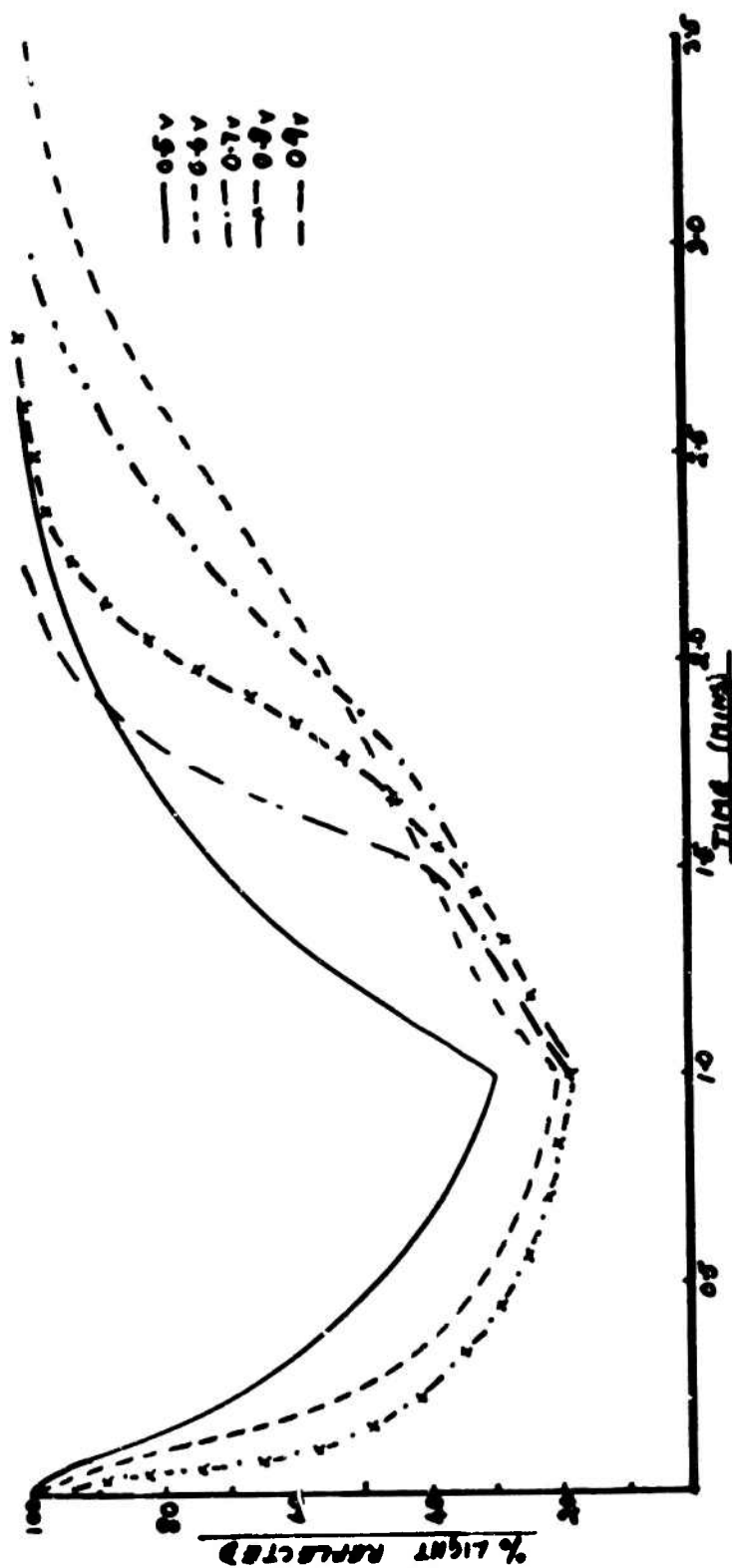


Fig. 64 Light reflected versus time curves for compound (I) (5%) with potassium bromide and hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.

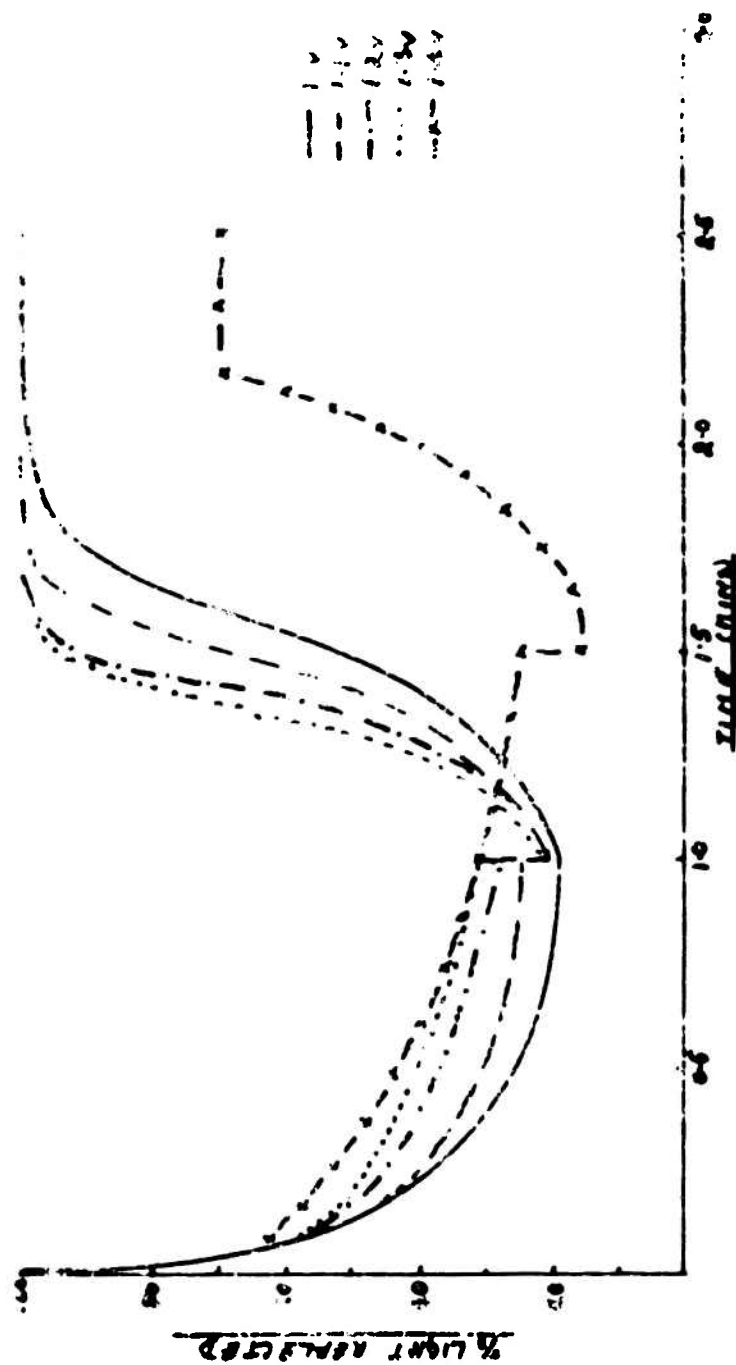


Fig. 65. Light scattered versus time curves for compound (I) (0.1%) with 10% potassium bromide and hydroquinone (0.01M) contained. A tin oxide transparent anode and a silver anode.

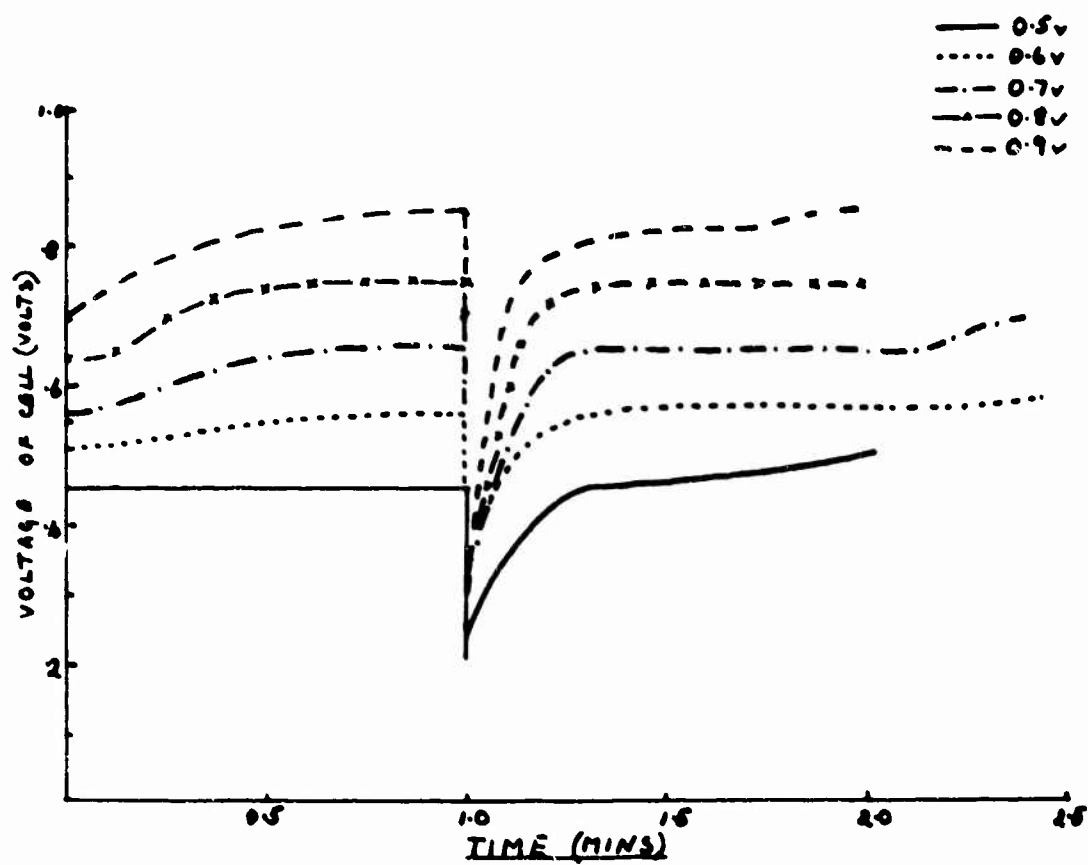
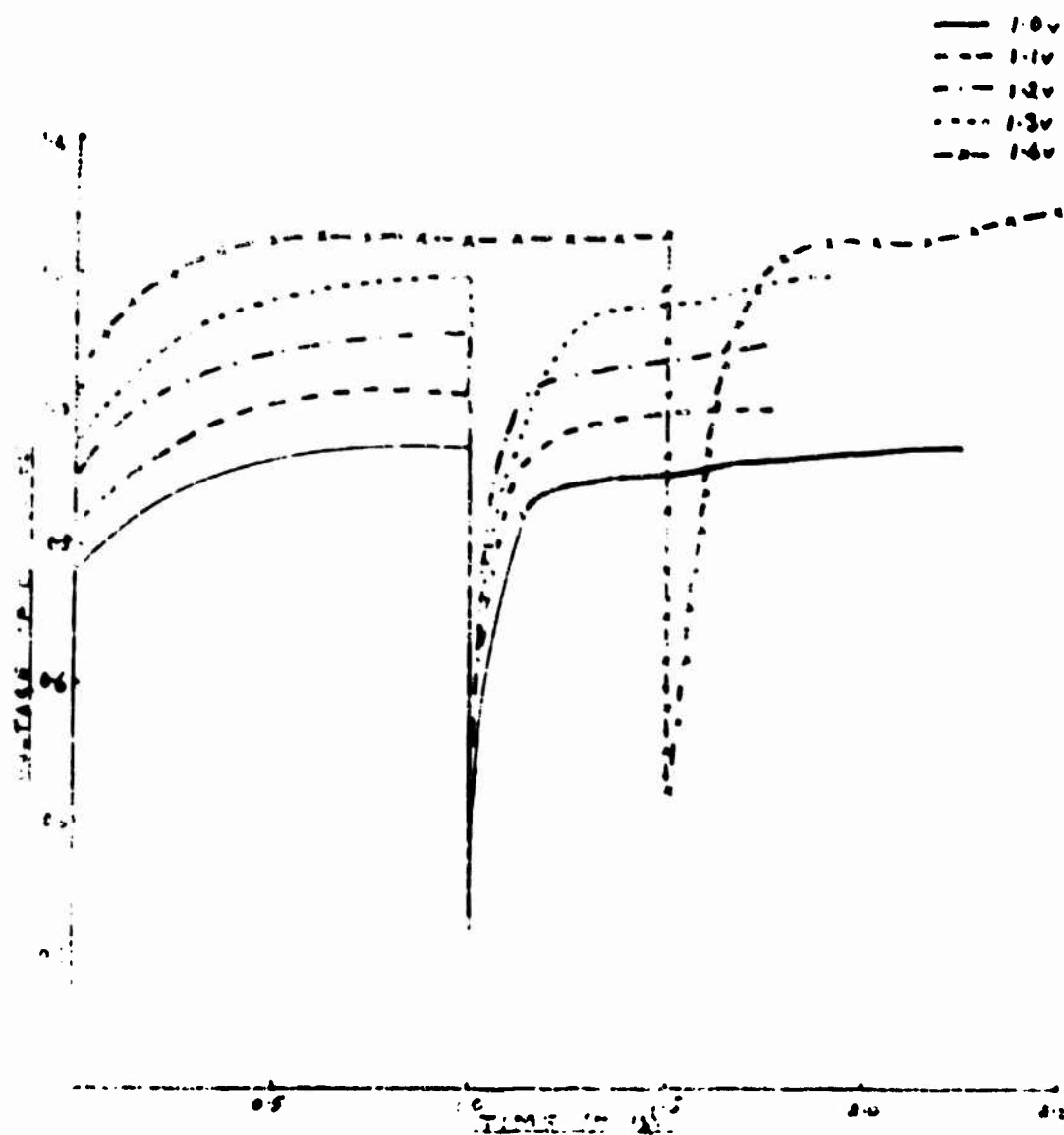


Fig. 66 Voltage versus time curves for compound (I) (5%) with potassium bromide and hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.



Voltage versus time curves for compound (I) (5%) with butyrate, bromide and hydroquinone (0.01M) continued. A tin oxide transparent cathode and a silver anode.

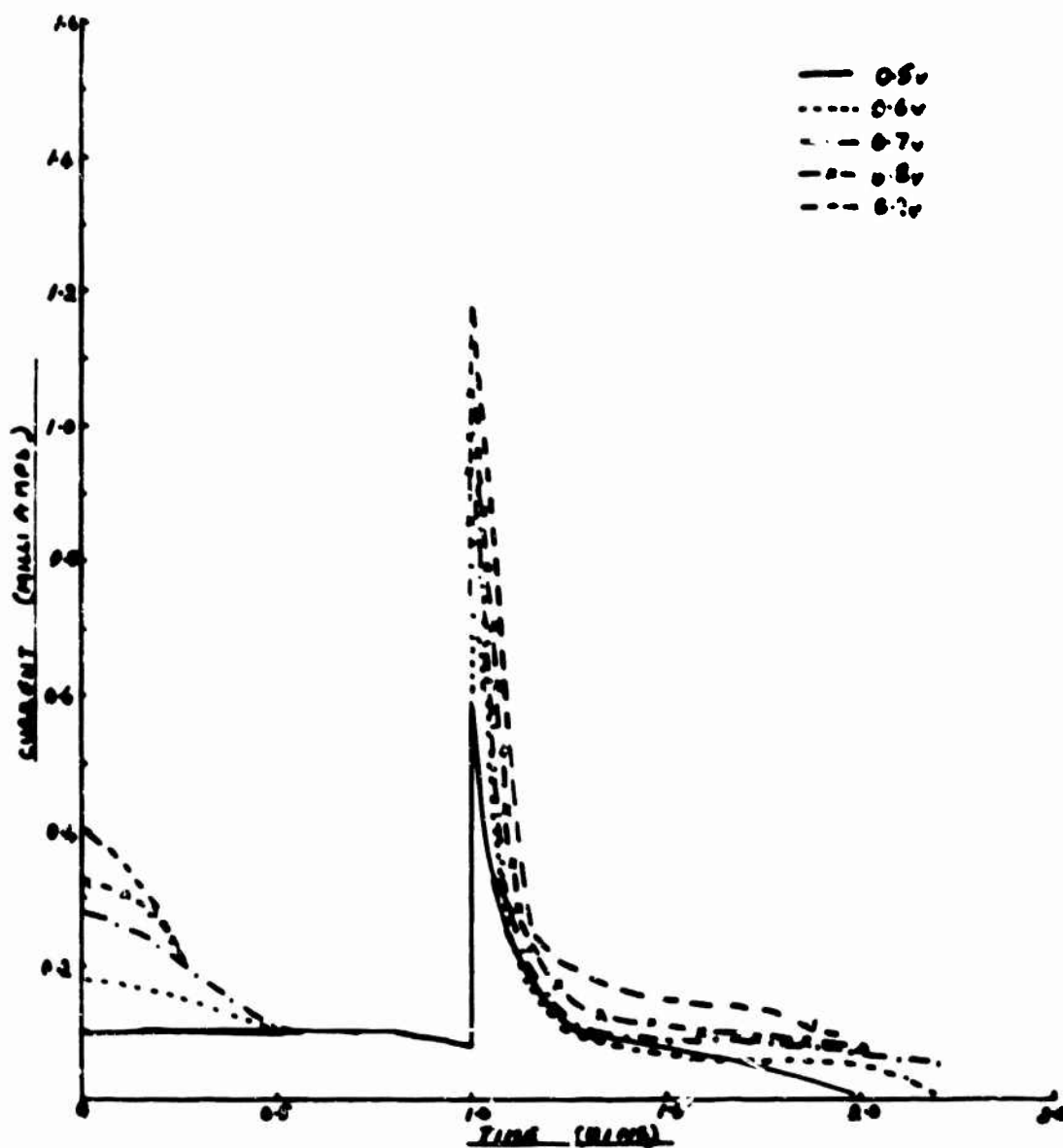


Fig. 68 Current versus time curves for compound (I) (5%) with potassium bromide and hydroquinone (0.01M). A tin oxide transparent cathode and a silver anode.

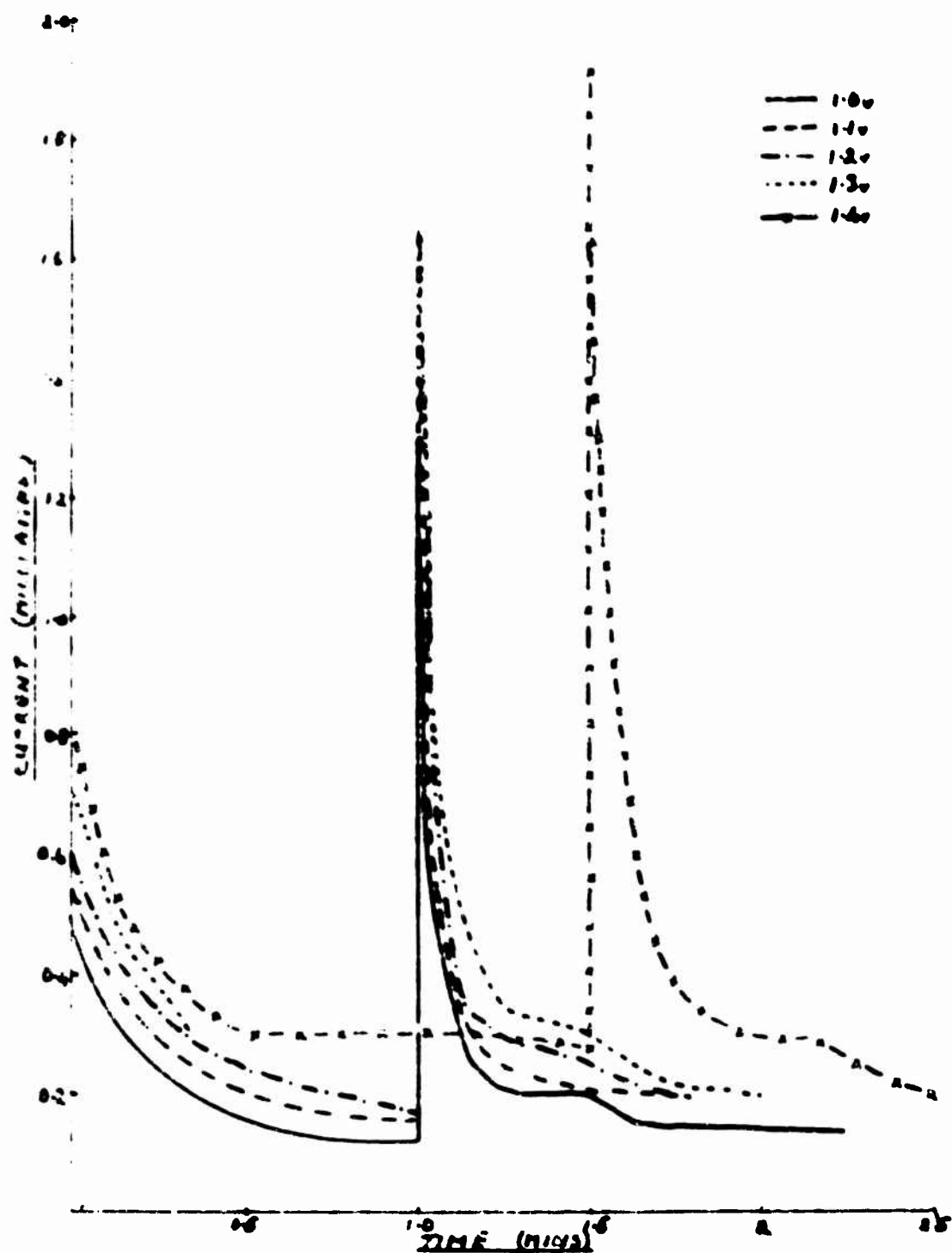


Fig. 69 Current versus time curves for compound (I) (5%) with potassium bromide and hydroquinone (0.01M) continued. A tin oxide transparent cathode and a silver anode.

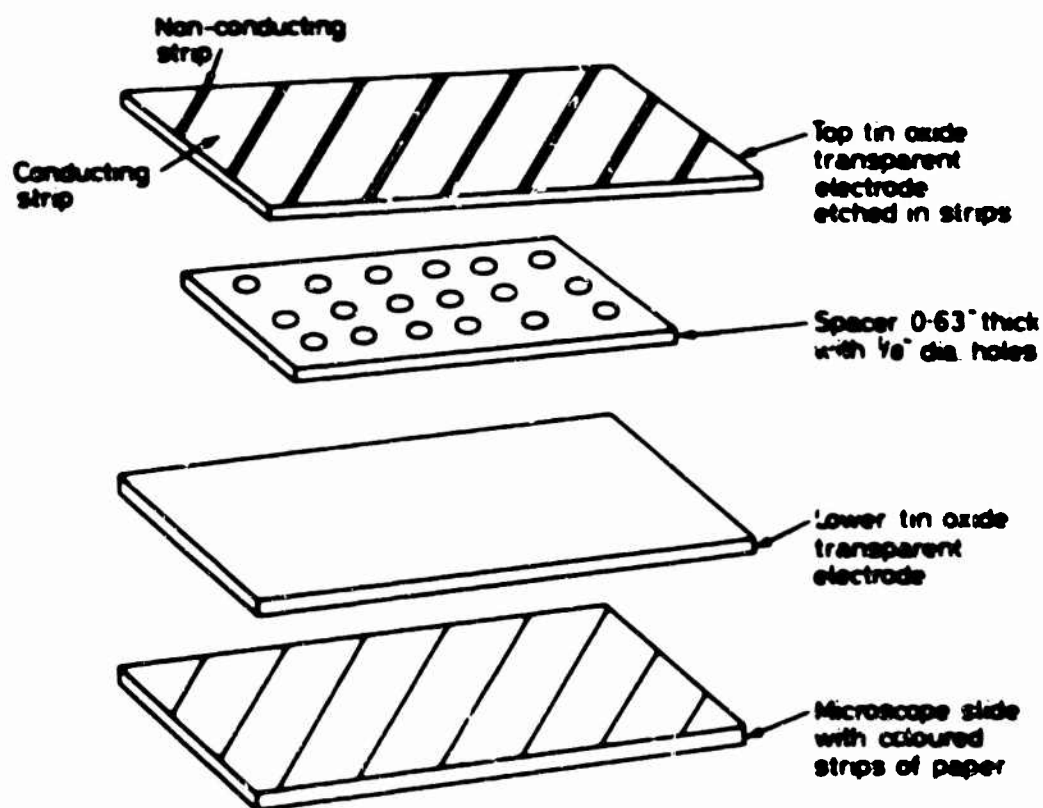


Fig.70 Display cell

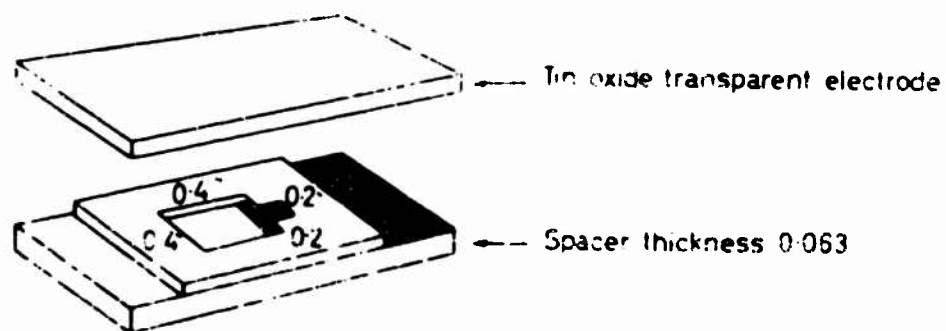


Fig.71 Cell with small area anode

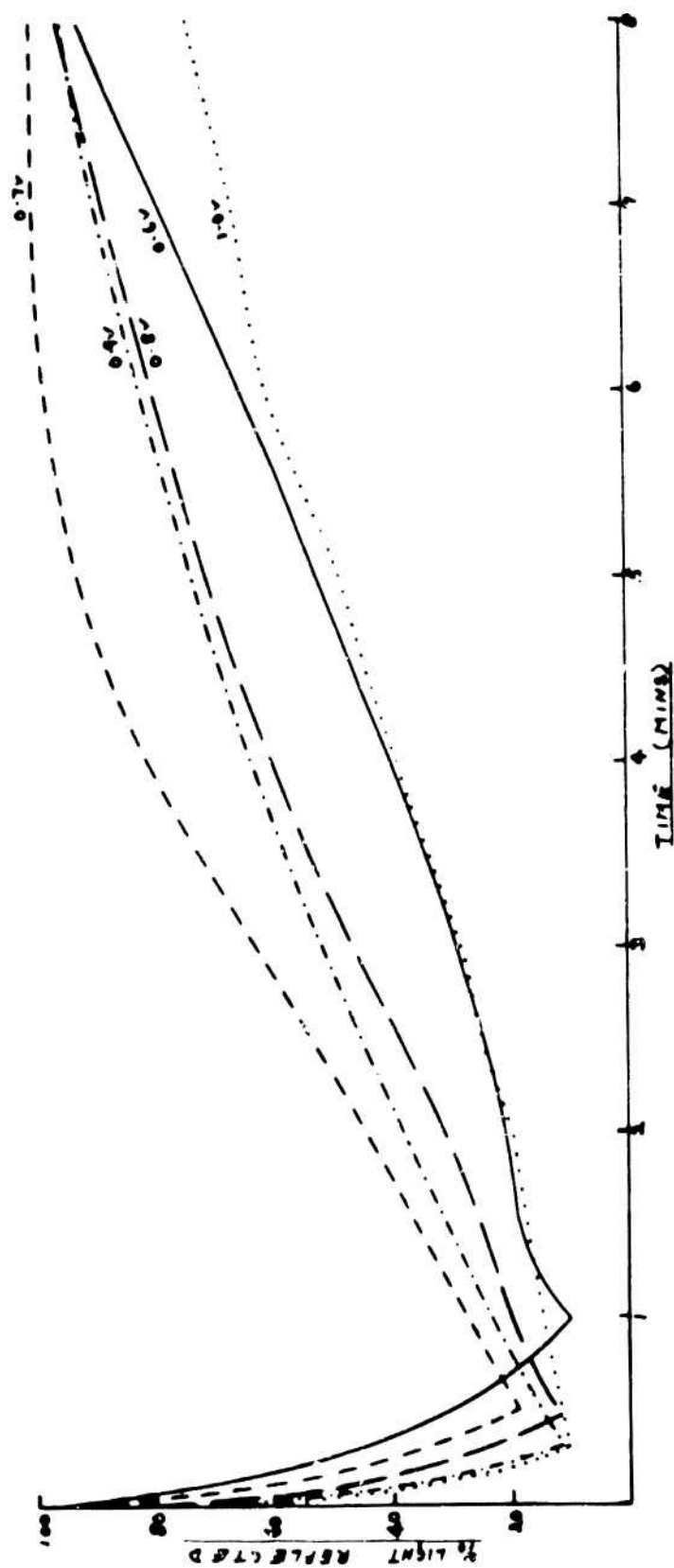


Fig. 72 Light reflected vs. time curves for compound (I) with ferrous ammonium sulphate. A tin oxide transparent cathode and a silver anode.

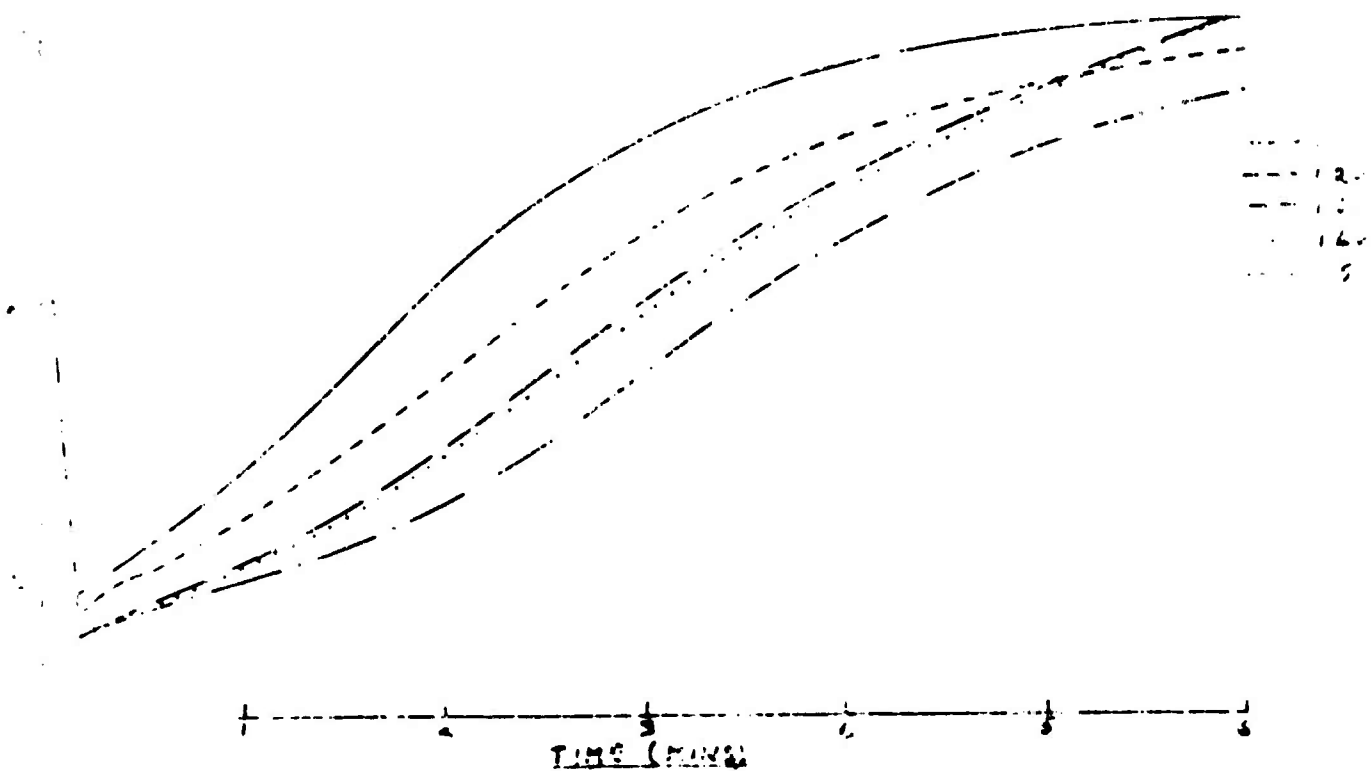


Figure 1. The effect of the concentration of the reactants on the rate of the reaction. The curves represent the rate of the reaction at different concentrations of the reactants.

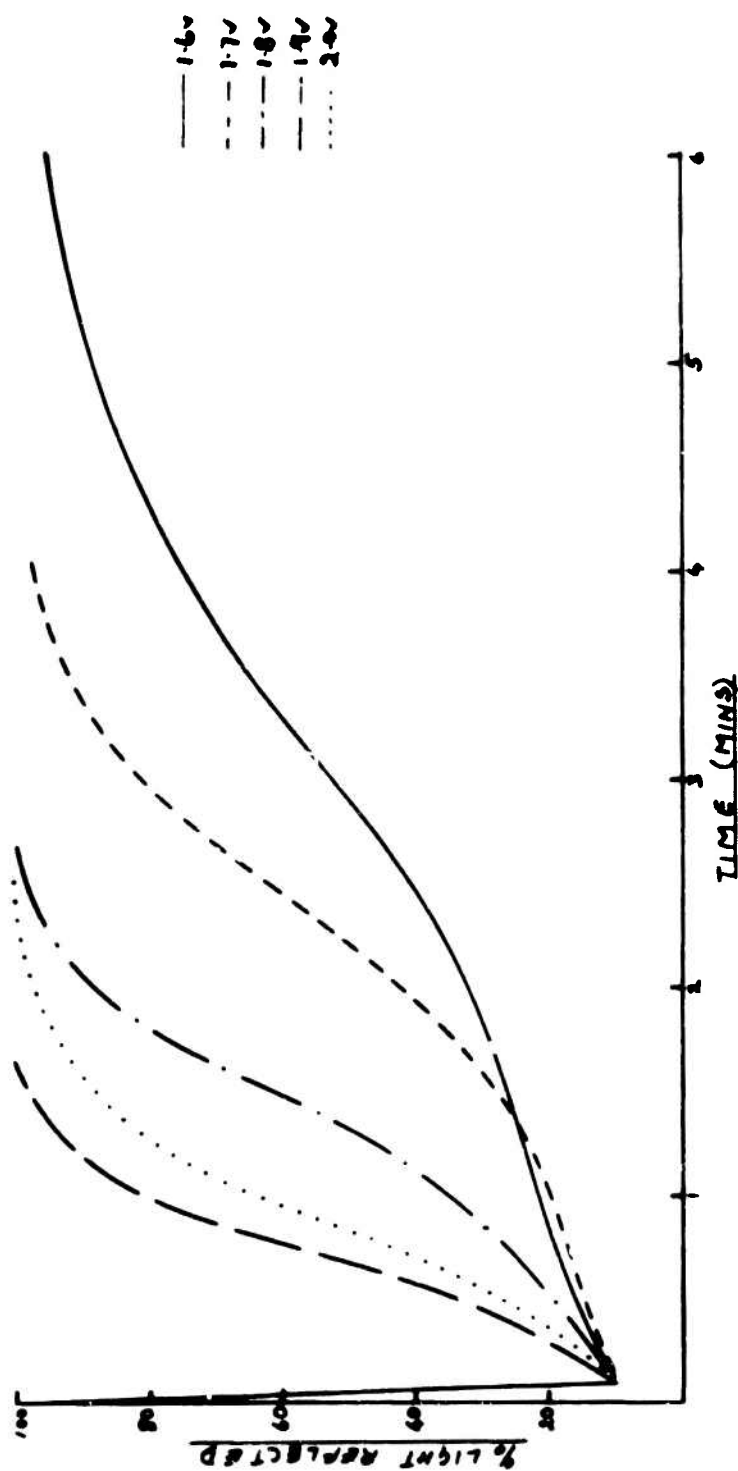


Fig. 74 Light reflected versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

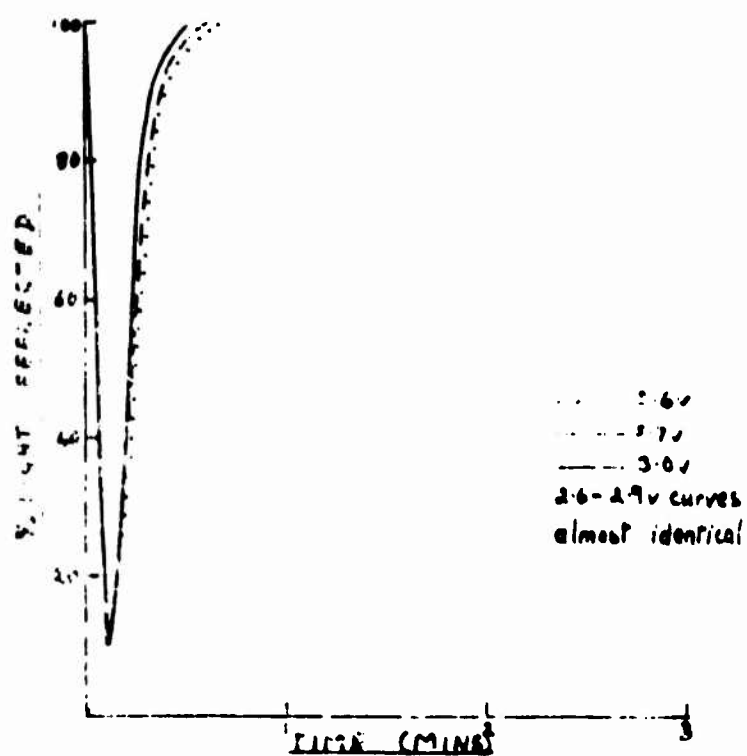
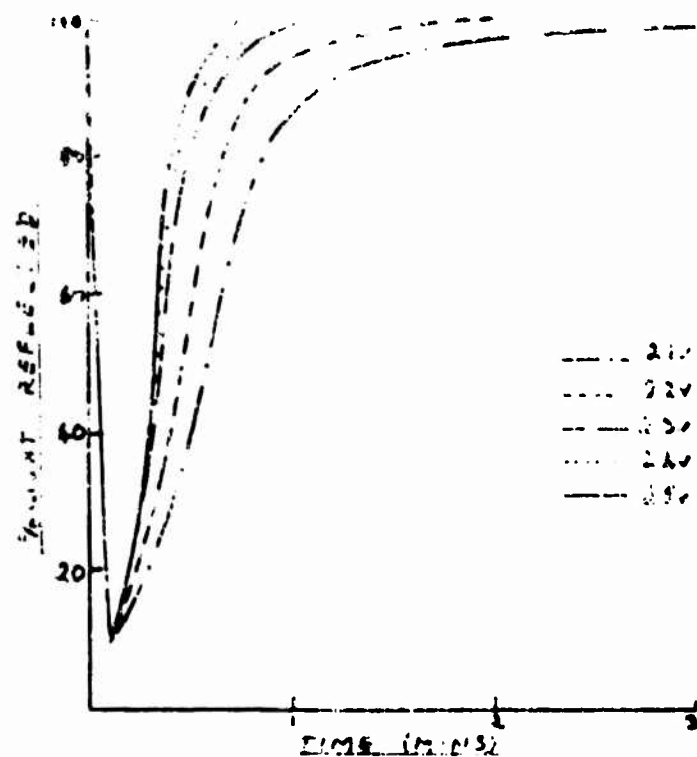


Fig. 7a. Light reflected versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and silver anode.

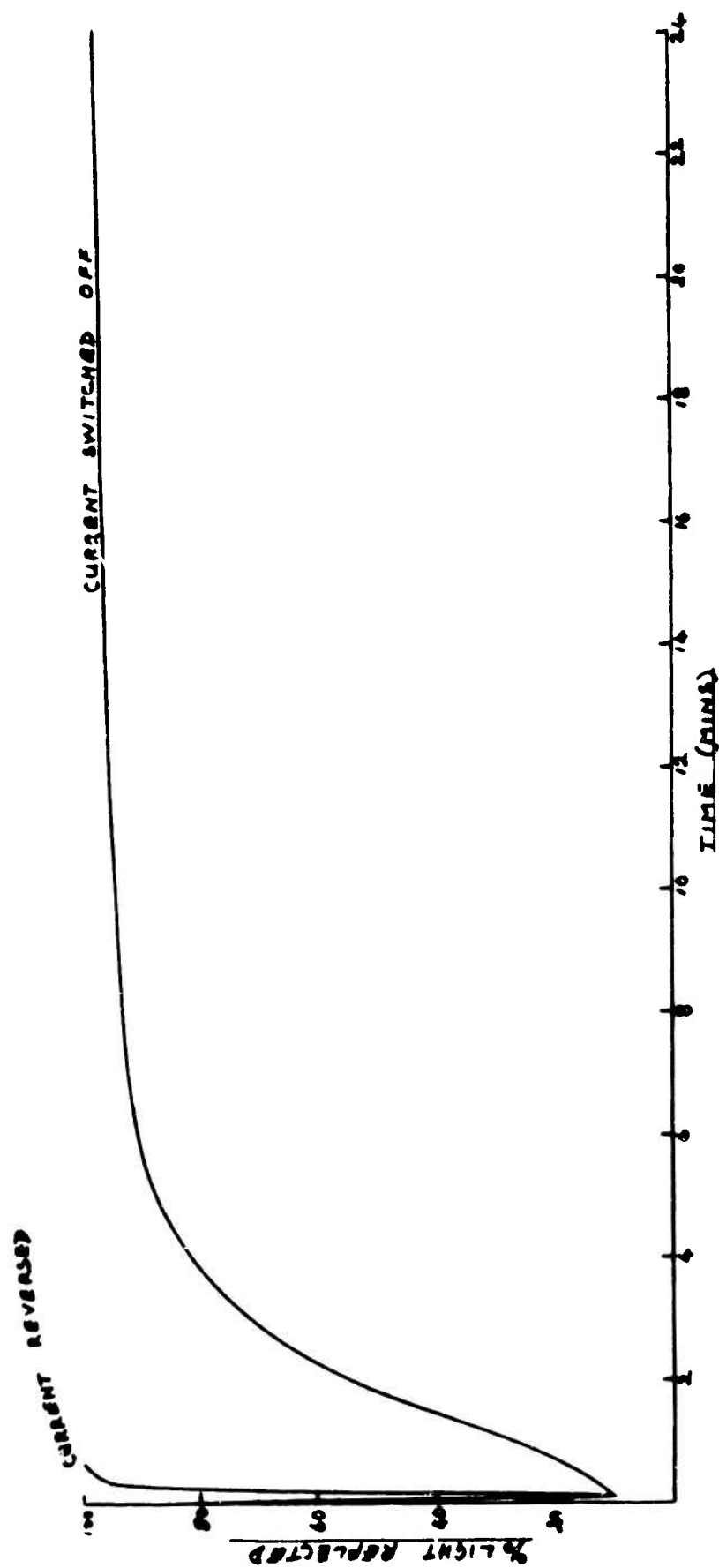


Fig. 76 Comparison of light reflected decay curves for compound (I) with ferrous ammonium sulphate. A tin oxide transparent cathode and a silver anode.

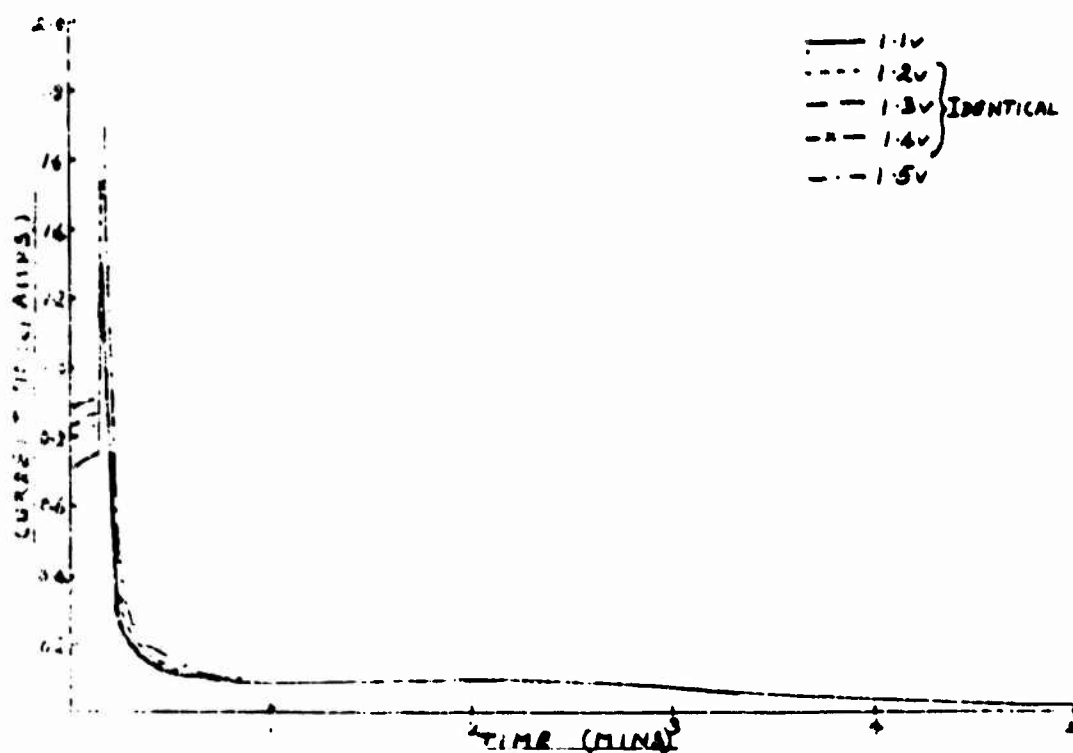
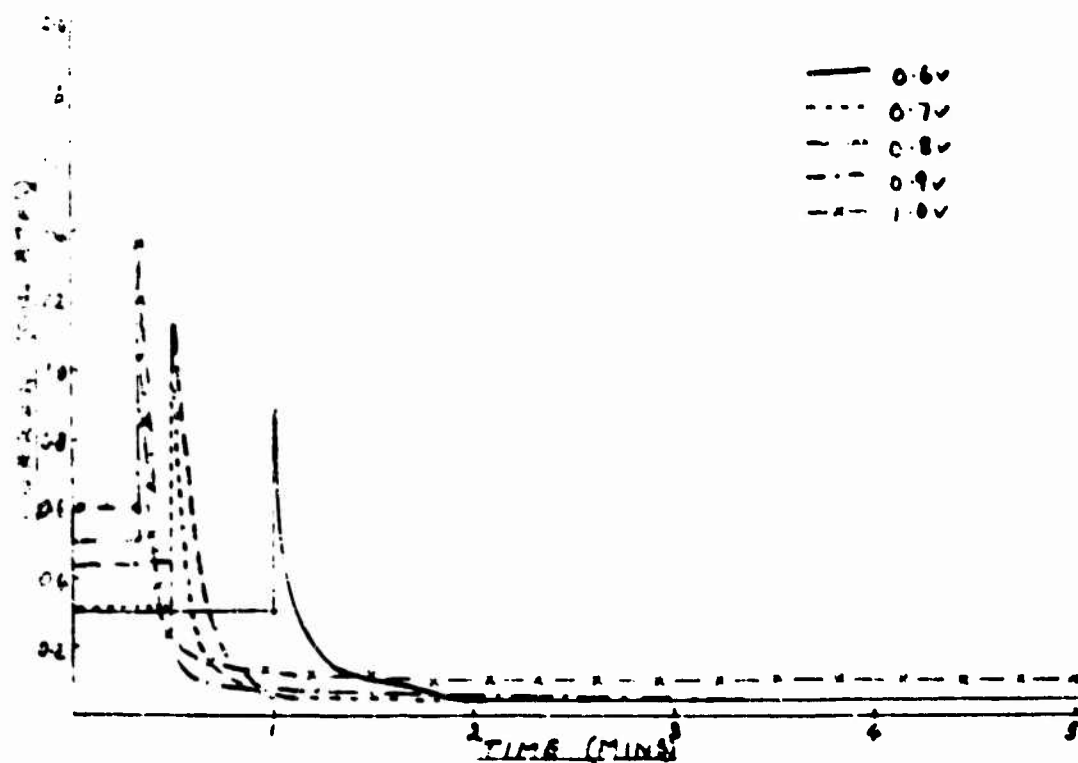


Fig. 77 Current versus time curves for compound (I) with ferrous ammonium sulphate. A tin oxide transparent cathode and a silver anode.

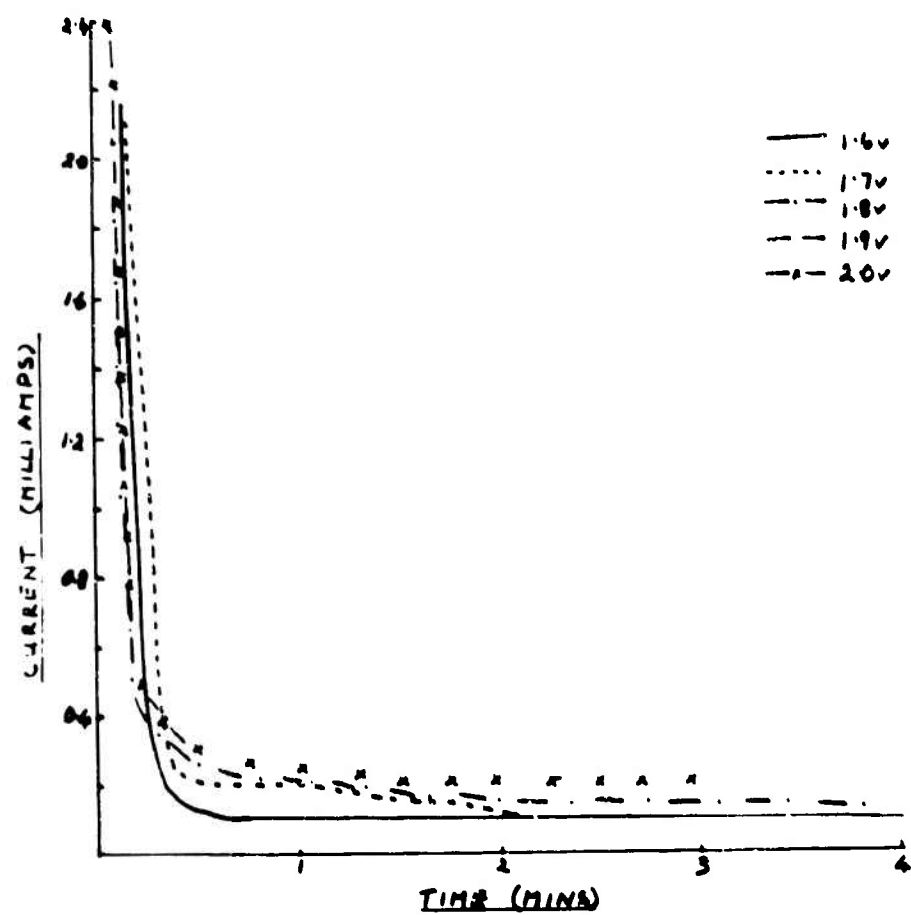


Fig. 76 Current versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

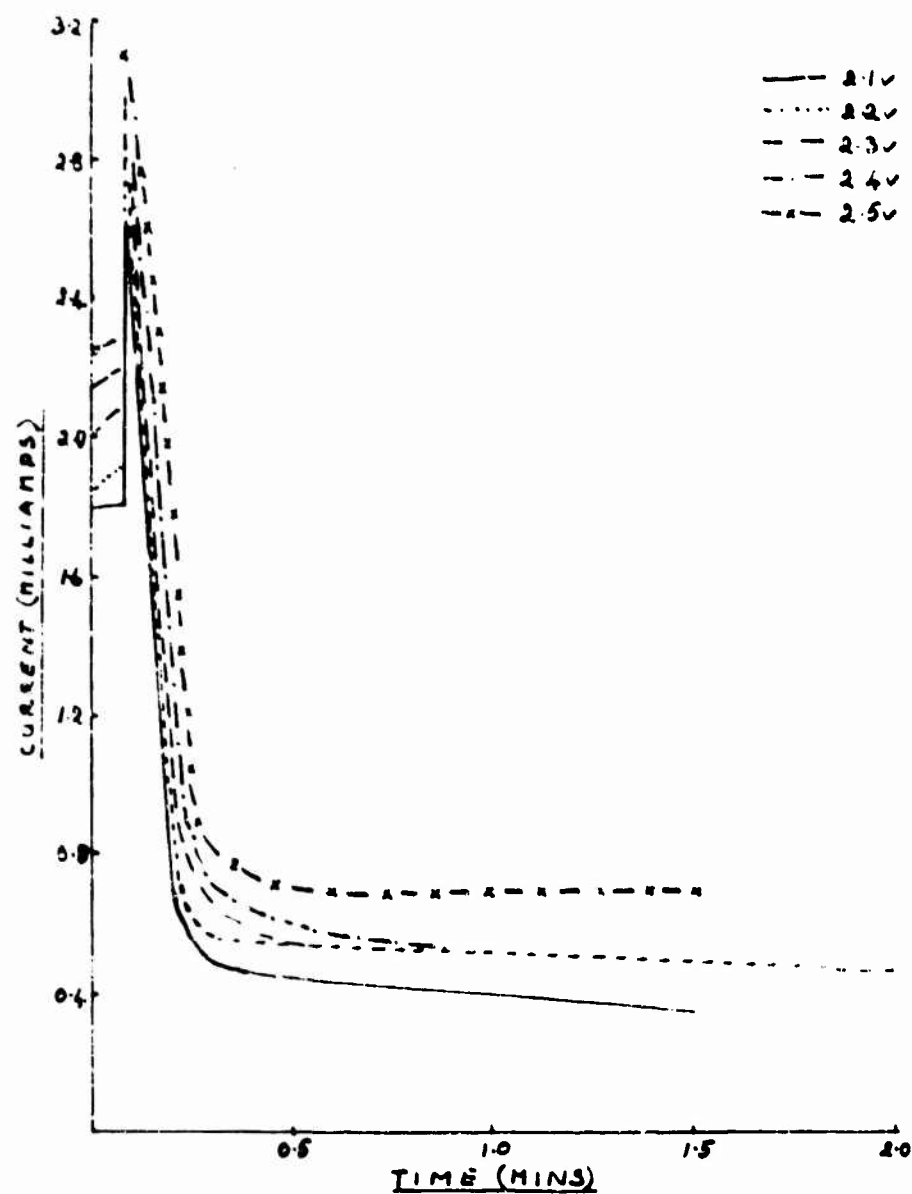


Fig. 79 Current versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

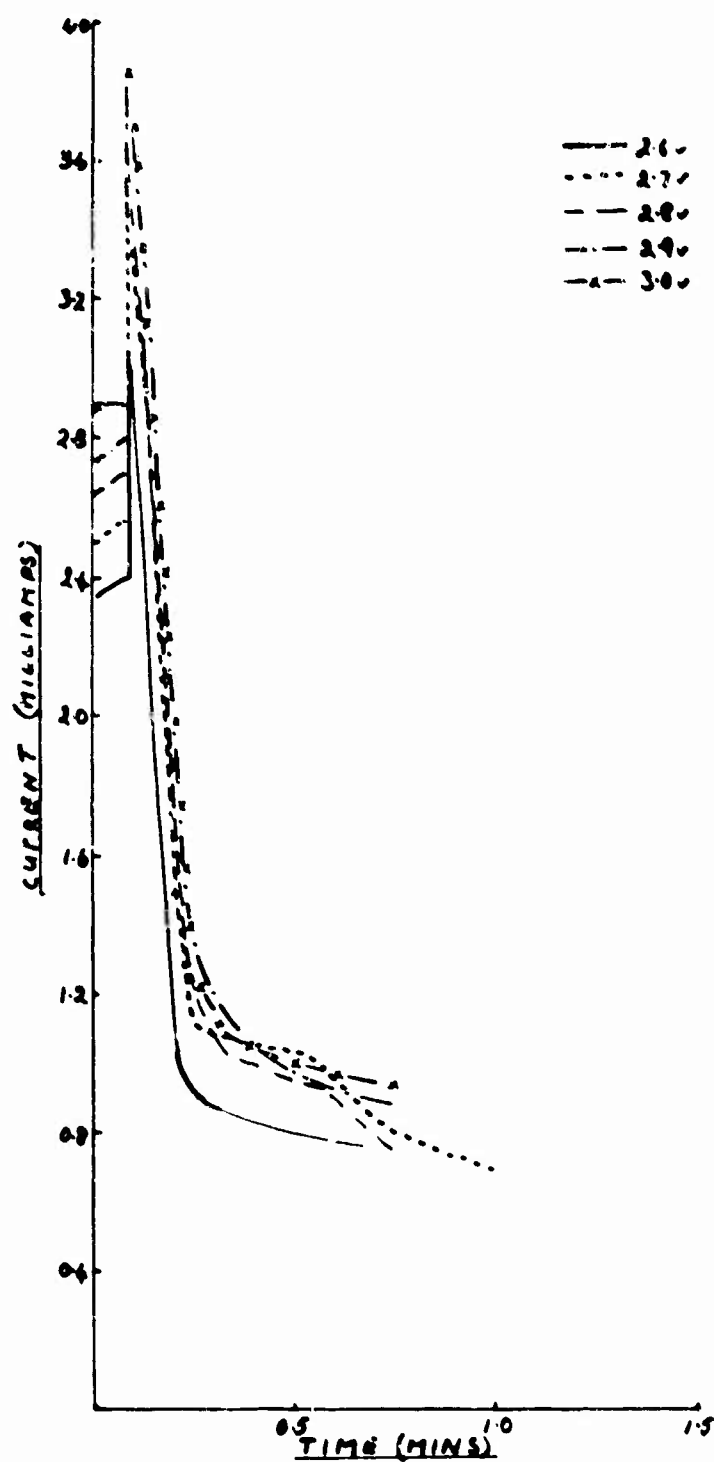


Fig. 80 Current versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

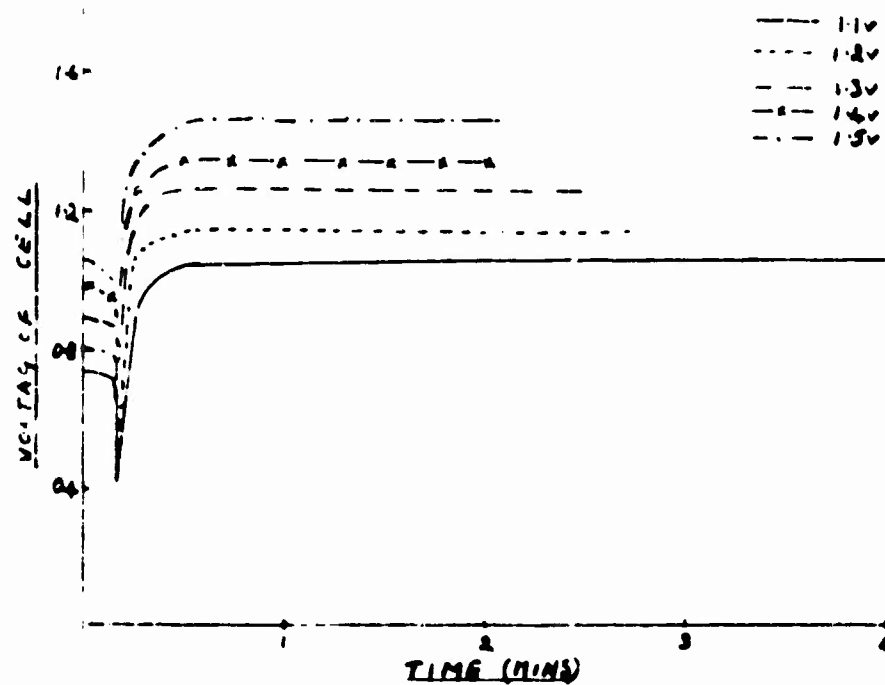
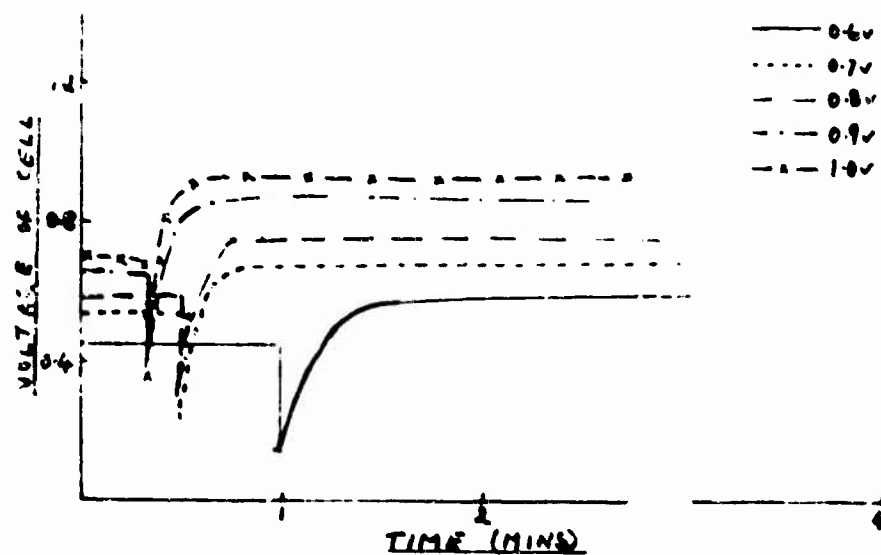


Fig. 11. Voltage versus time curves for compound (I) with ferrous ammonium sulphate. A tin oxide transparent cathode and a silver anode.

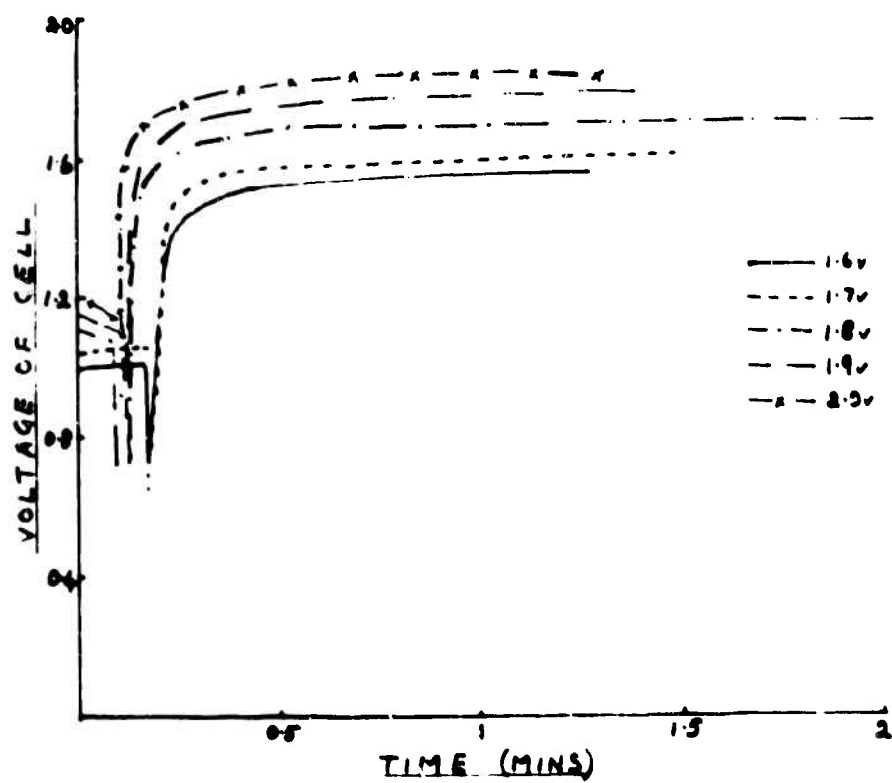


Fig. 62 Voltage versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

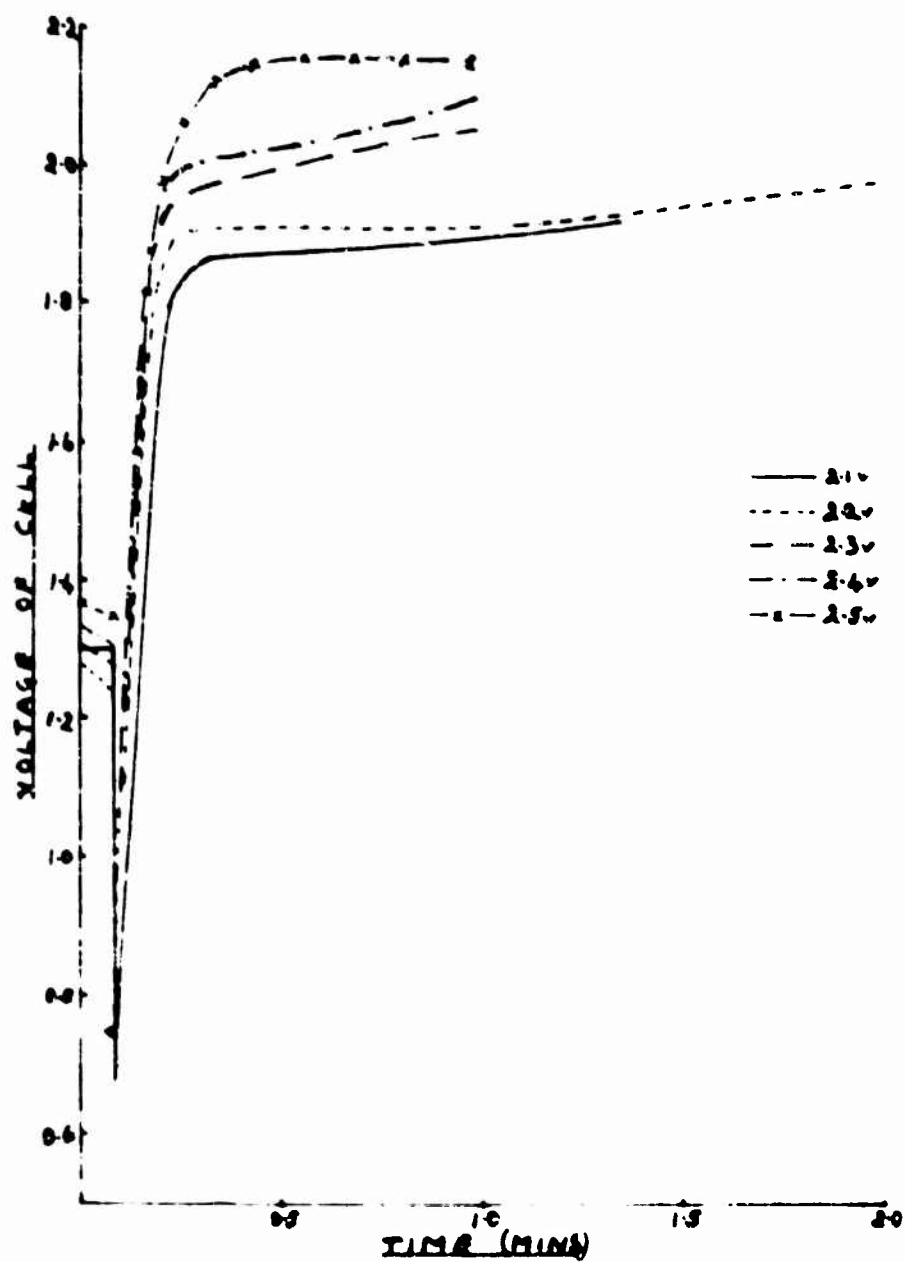


Fig. 23 Voltage versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode

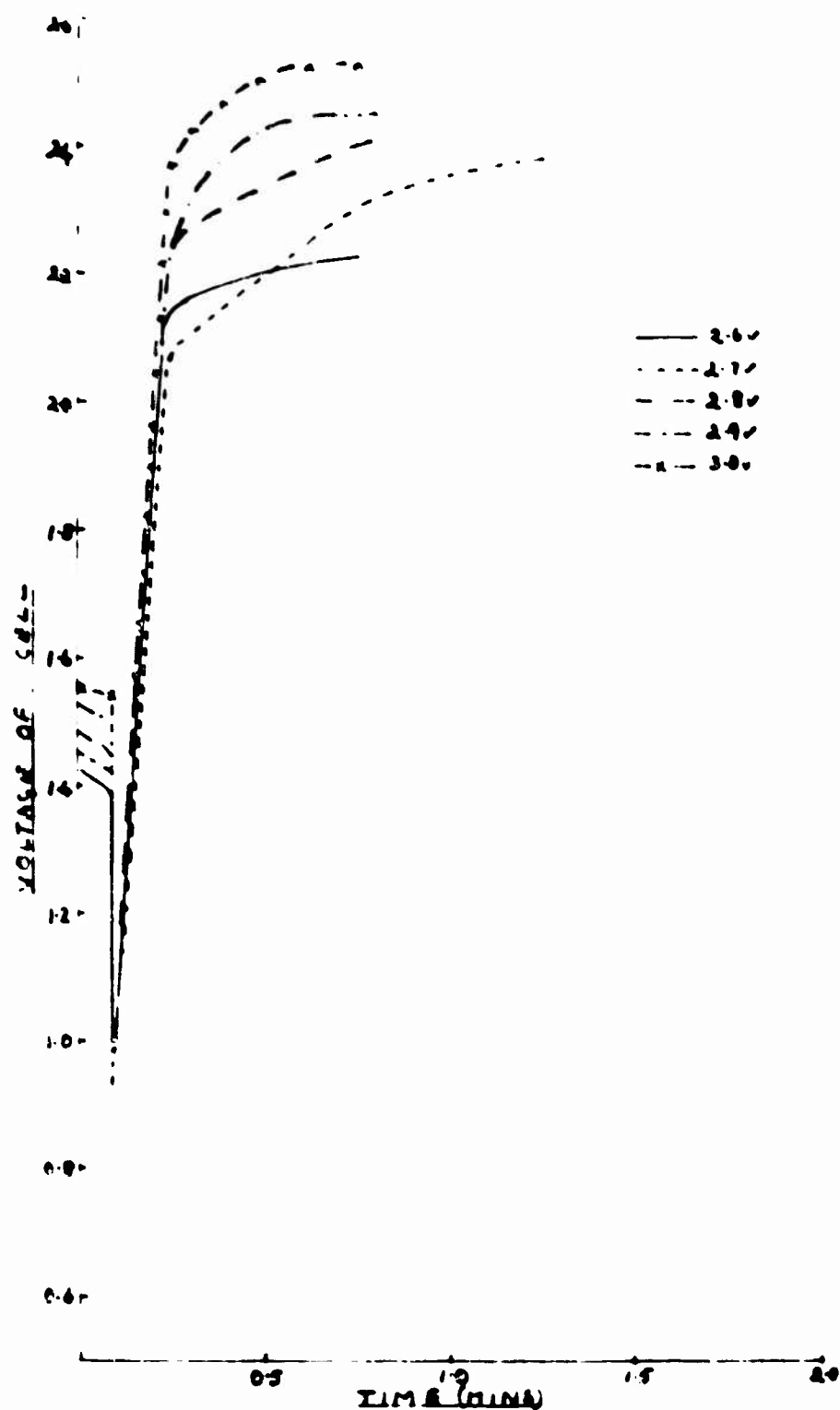


Fig. 64. Voltage versus time curves for compound (I) with ferrous ammonium sulphate continued. A tin oxide transparent cathode and a silver anode.

Fig. 55

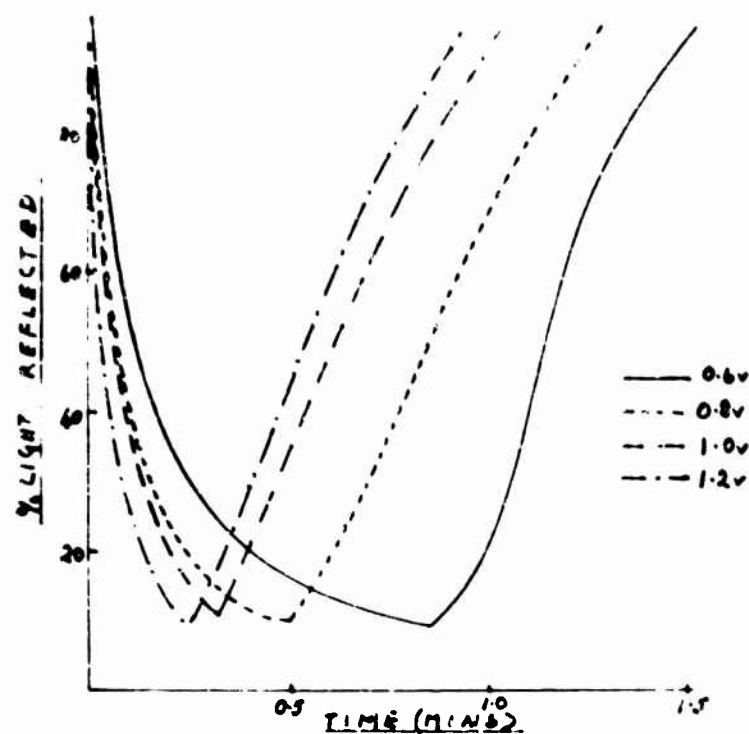


Fig. 56

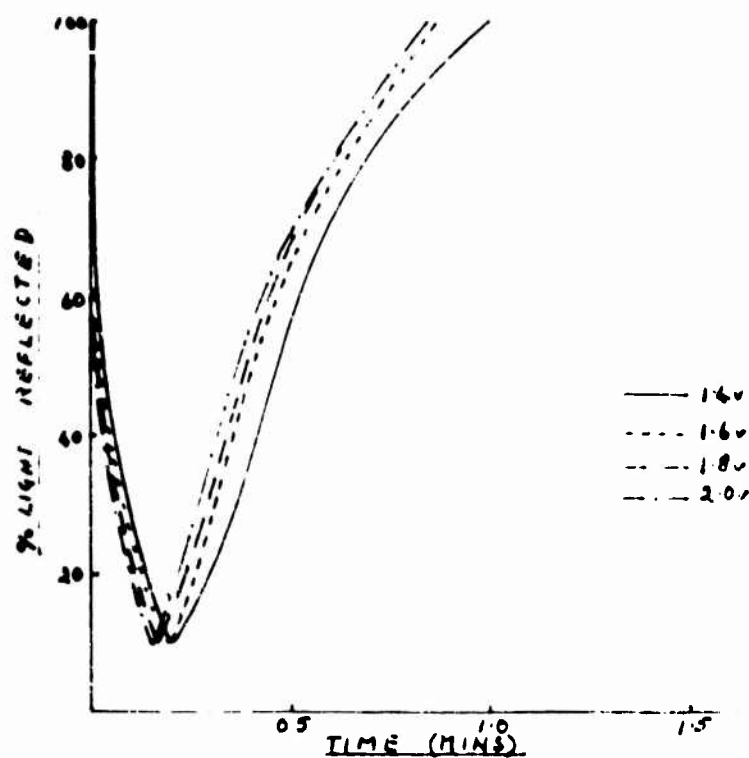
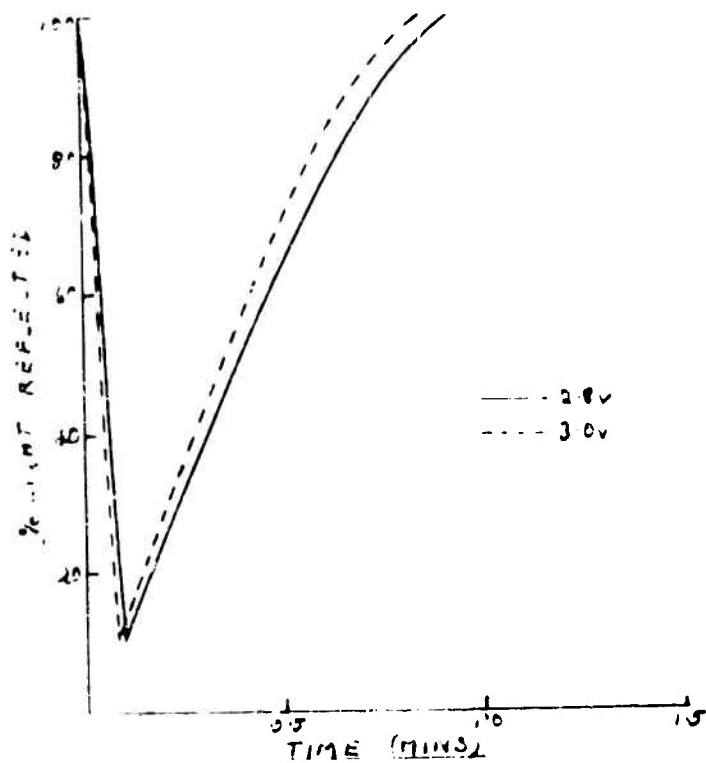
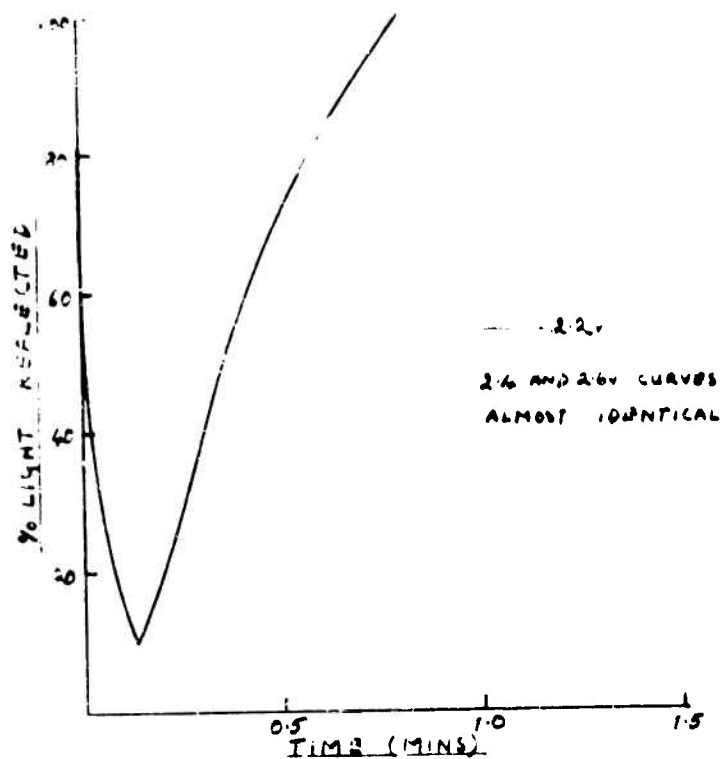


Fig. 55 and 56 Light reflected versus time curves for compound (I) with compound (A) and sodium sulphite. A tin oxide transparent cathode and a silver anode.



The curves show that the percentage of light reflected increases with time, and that the rate of increase is higher for higher potentials. The 2.8V and 3.0V curves are very similar, indicating that the system is nearly saturated at these potentials.

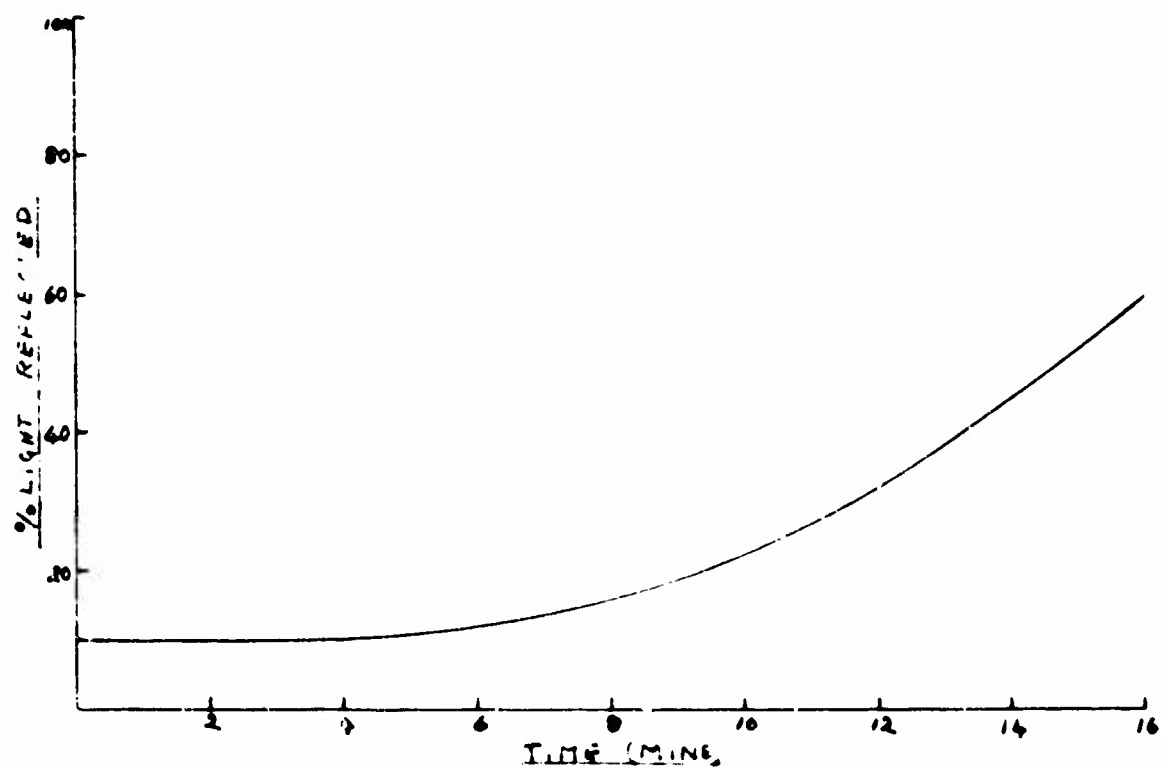
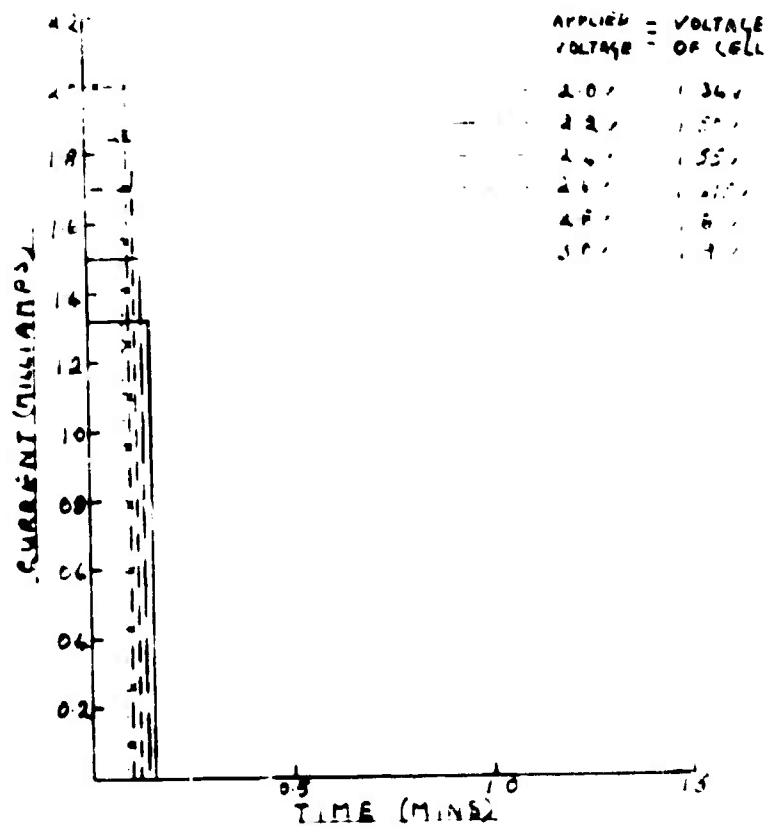
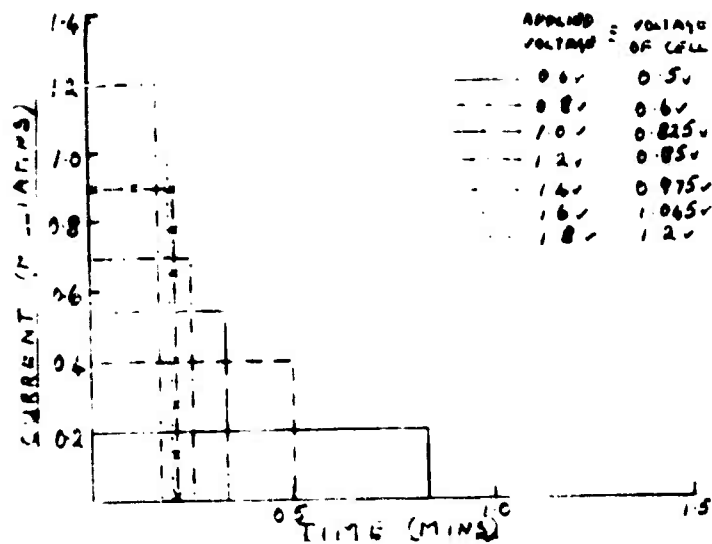
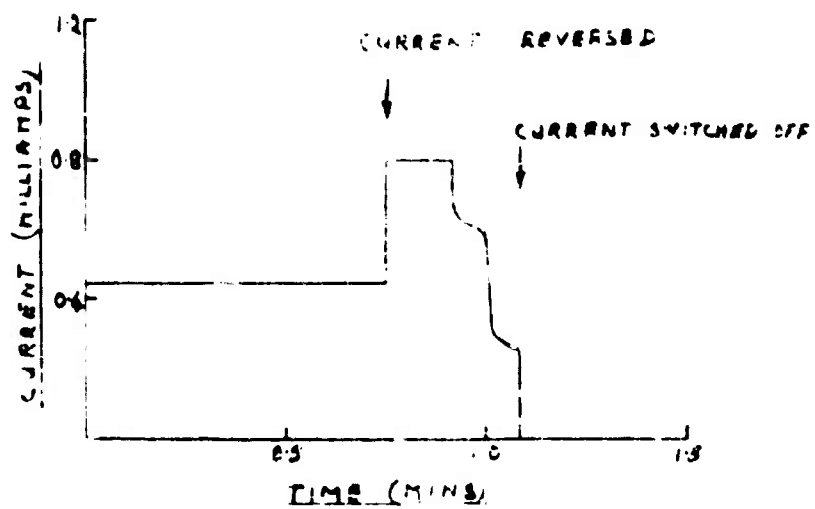


Fig. 1. The effect of time on the percentage of light reflected by a surface of water.





The current was reversed at 0.5 minutes and switched off at 1.0 minutes. The current was then reversed again at 1.5 minutes and switched off at 2.0 minutes.

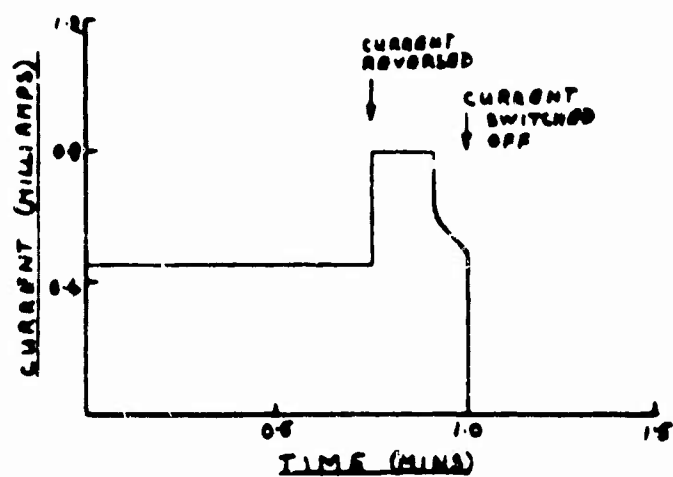


Fig. 23. Current-time curve for compound (I) with compound (A) and sodium sulphite. Current reversed at 1.0 min. light reflected. A tin oxide transparent cathode and a silver anode.

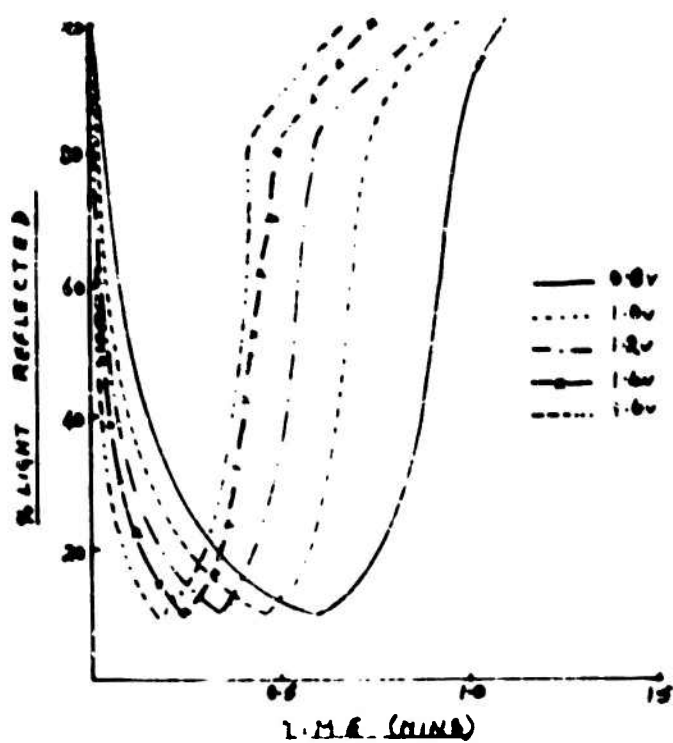


Fig. 94 Light reflected versus time curves for compound (I) with compound (A) and sodium sulphite (0.02M). A tin oxide transparent cathode and a silver anode

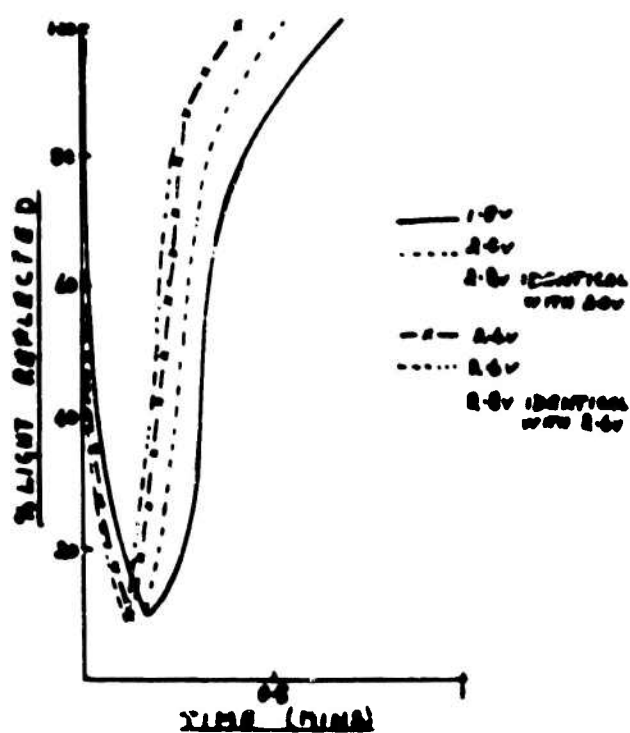


Fig. 95 Light reflected versus time curves for compound (I) with compound (A) and sodium sulphite (0.02M) continued. A tin oxide transparent cathode and a silver anode.

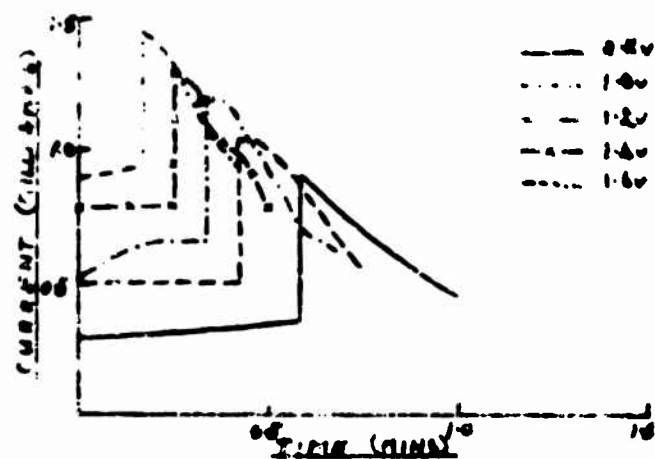
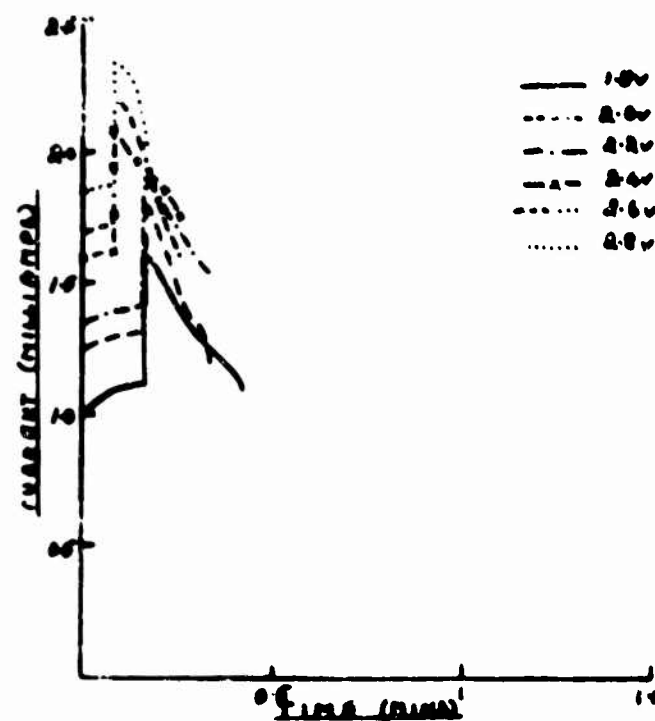


Fig. 97



Figs. 96 and 97 Current versus time curves for compound (i) with compound (A) and sodium sulphite (0.02M). A tin oxide transparent cathode and a silver anode.

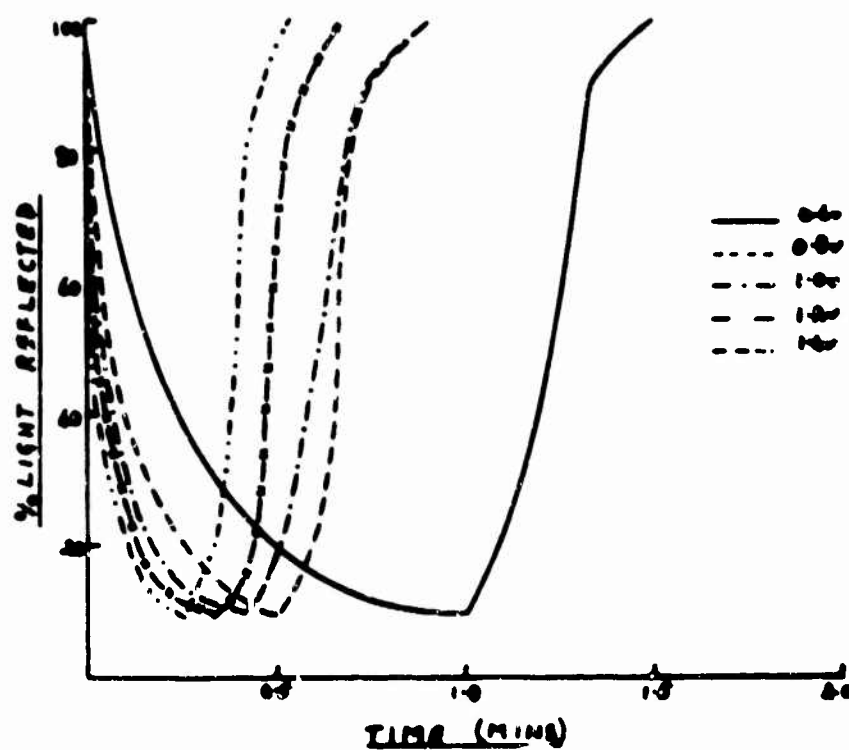


Fig. 98 Light reflected versus time curves for compound (I) with compound (A) and sodium sulphite (0.1M). A tin oxide transparent cathode and a silver anode.

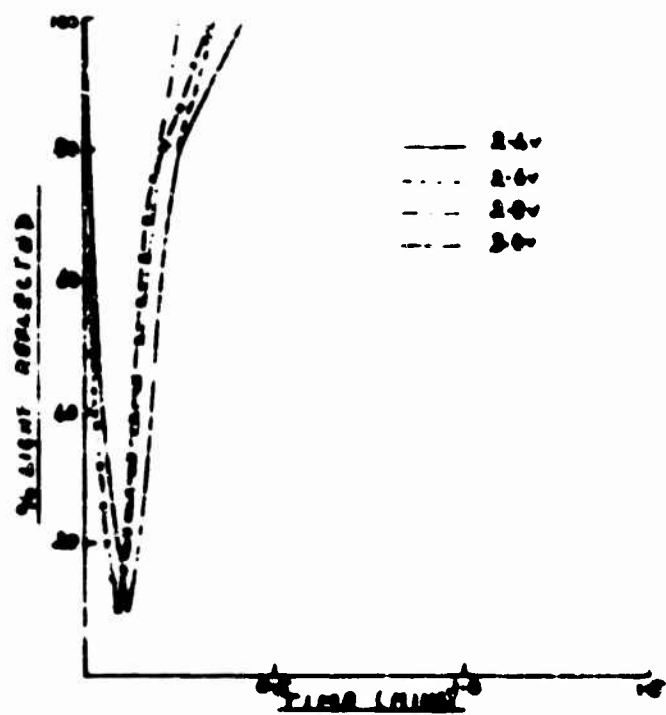
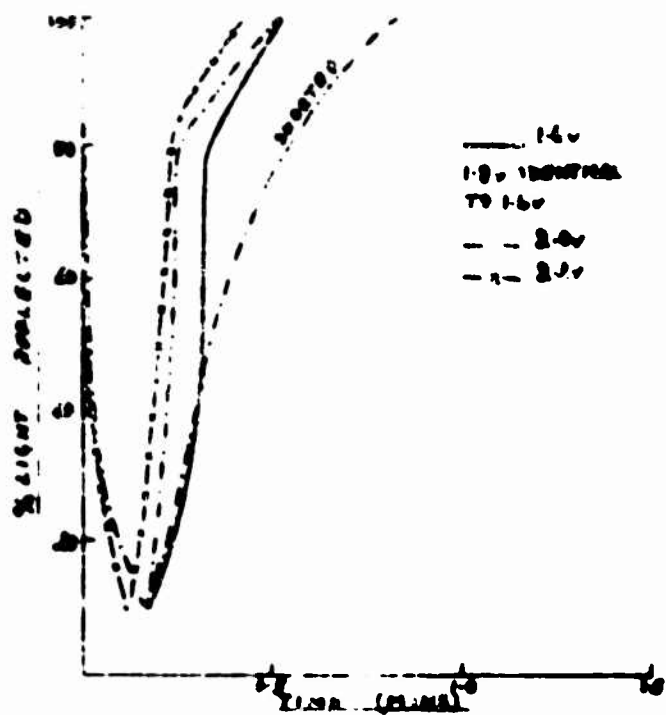


Fig. 95 Light reflected versus time curves for compound (I) with compound (A), and sodium sulphite (0.1M) continued. A tin oxide transparent cathode and silver anode.

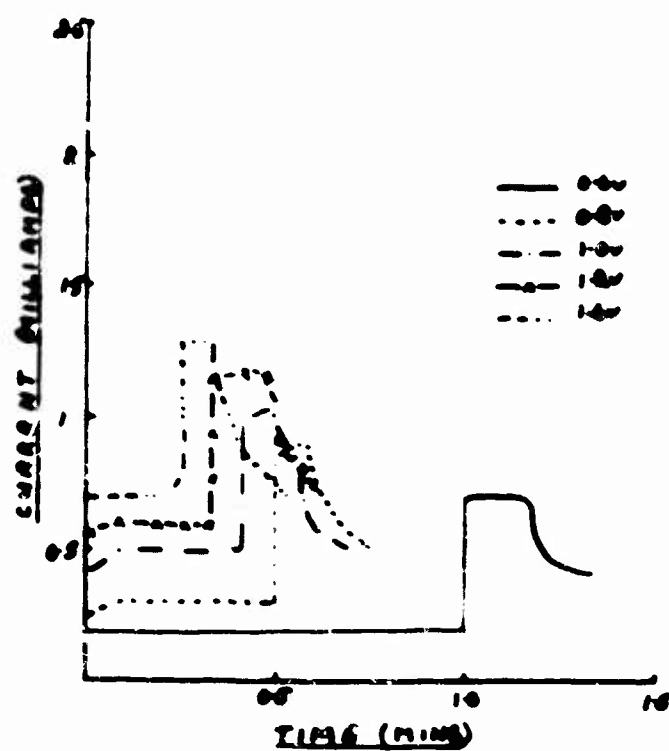


Fig. 100 Current versus time curves for compound (I) with compound (A) and sodium sulphite (0.1M). A tin oxide transparent cathode and a silver anode.

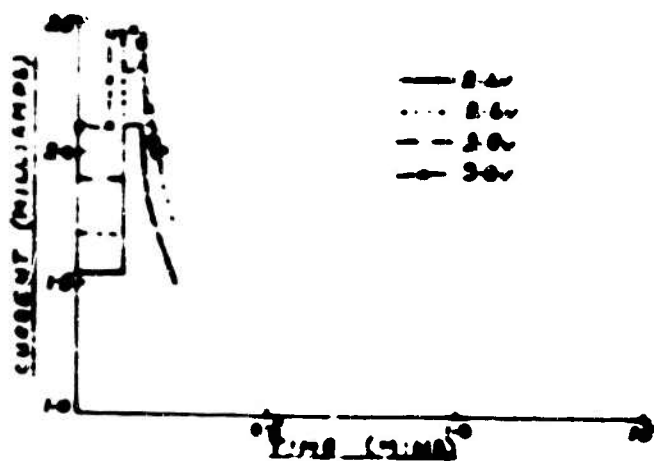
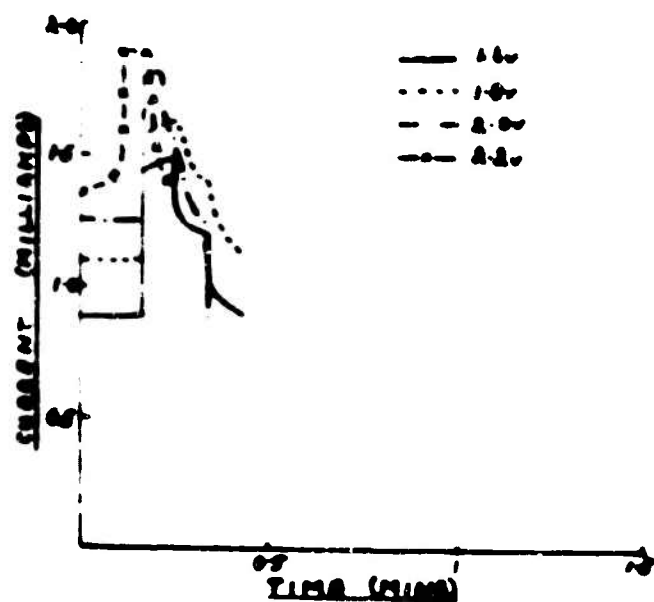


Fig. 10] Current versus time curves for compound (I) with compound (A) and sodium sulphite (0.1M) continued. A: in oxide transparent cathode and a silver anode

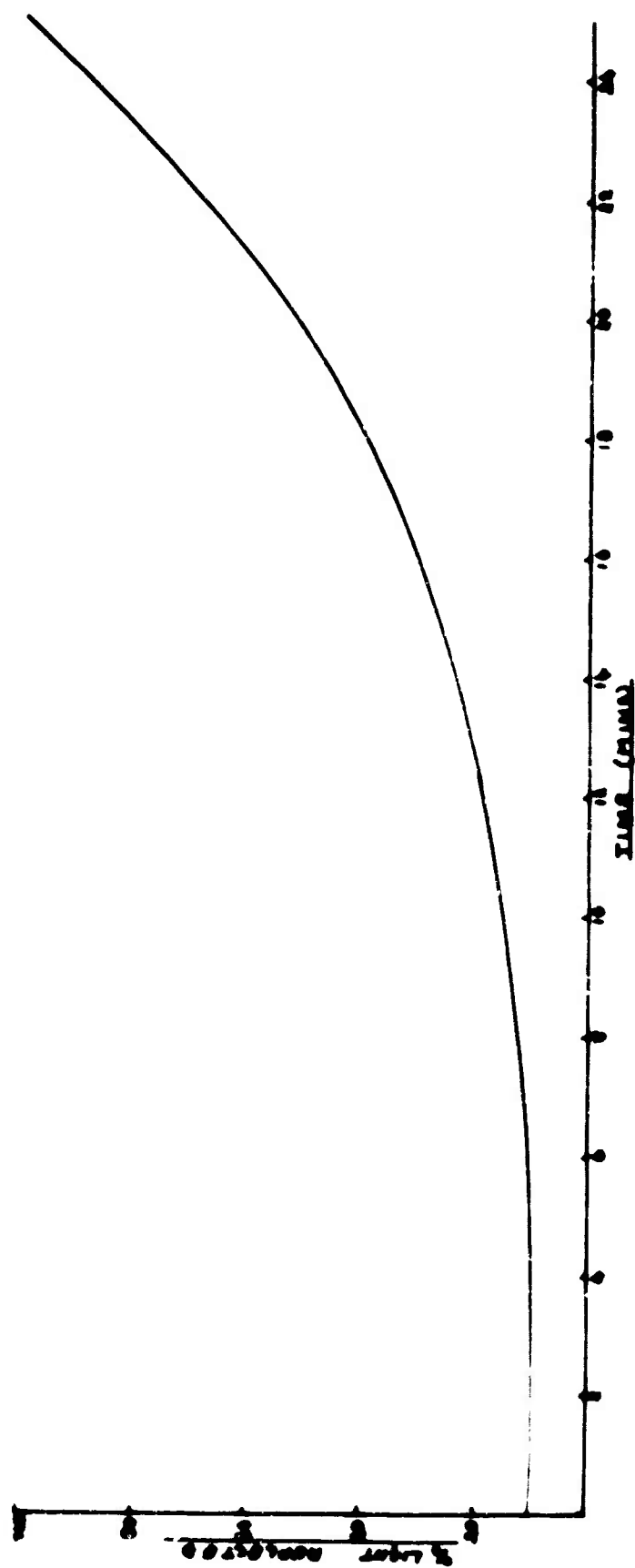


Fig. 102 Light reflected decay curve for compound (I) with compound (A) and sodium sulphite (0.1M). A tin oxide transparent cathode and a silver anode.

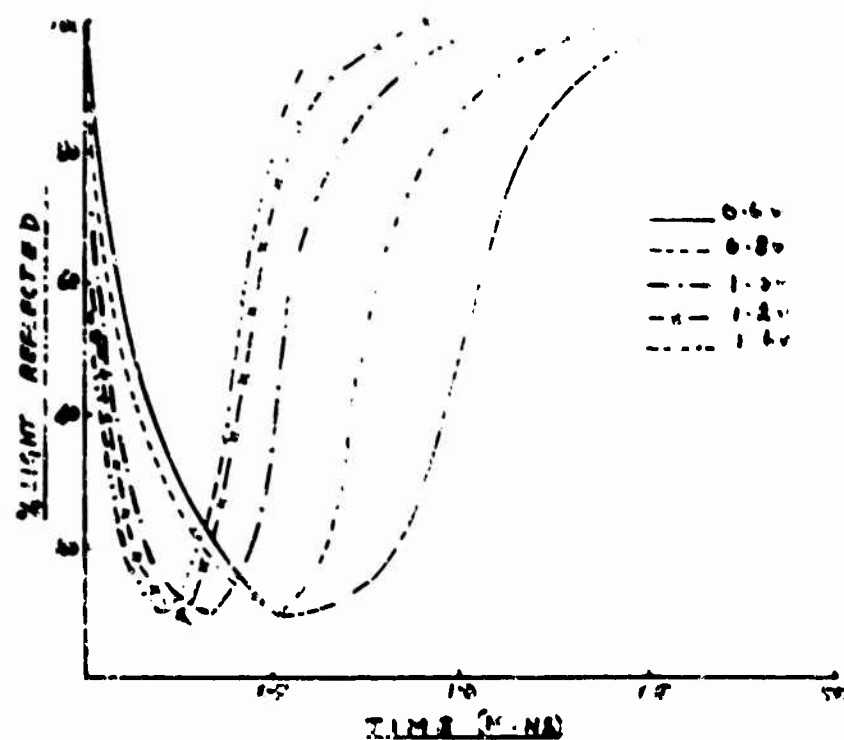


Fig. 103 Light reflected versus time curves for compound (I) with sodium sulphite (0.02M). A tin oxide transparent cathode and a silver anode.

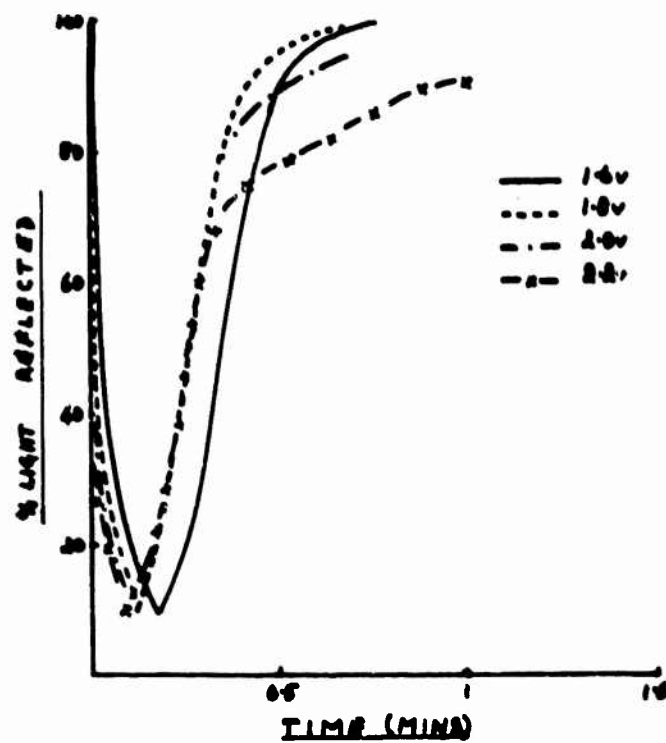


Fig. 104 Light reflected versus time curves for compound (I) and sodium sulphite (0.02M) continued. A tin oxide transparent cathode and a silver anode.

Fig. 105

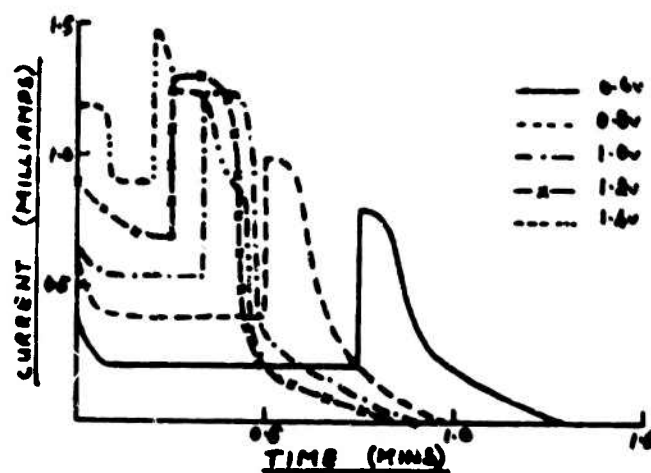
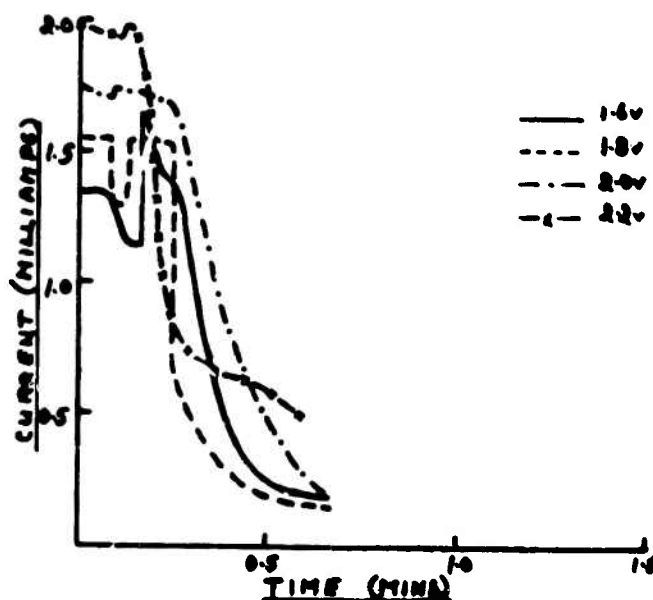


Fig. 106



Figs. 105 and 106 Current versus time curves for compound (I) and sodium sulphite (0.02M). A tin oxide transparent cathode and a silver anode.

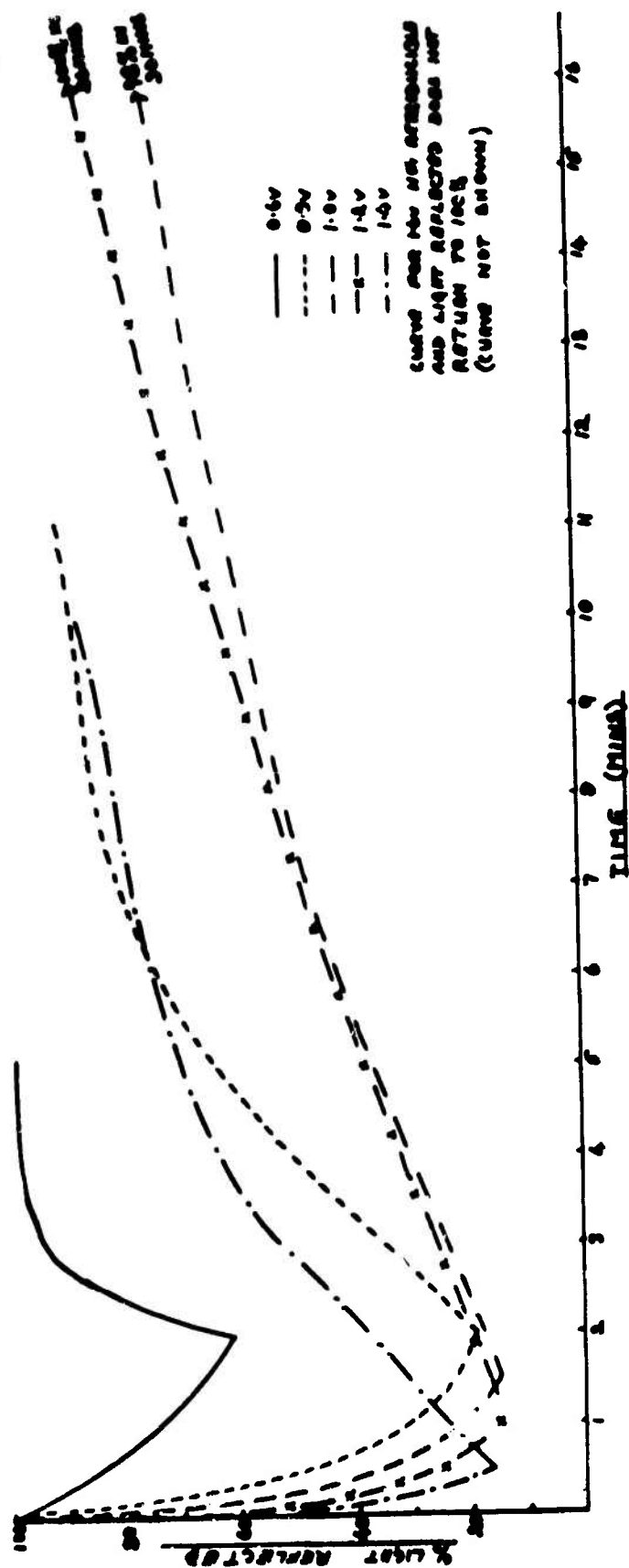


Fig. 107 Light reflected versus time curves for heptyl viologen dibromide with compound (A) and sodium sulphite. A tin oxide transparent cathode and a silver anode.

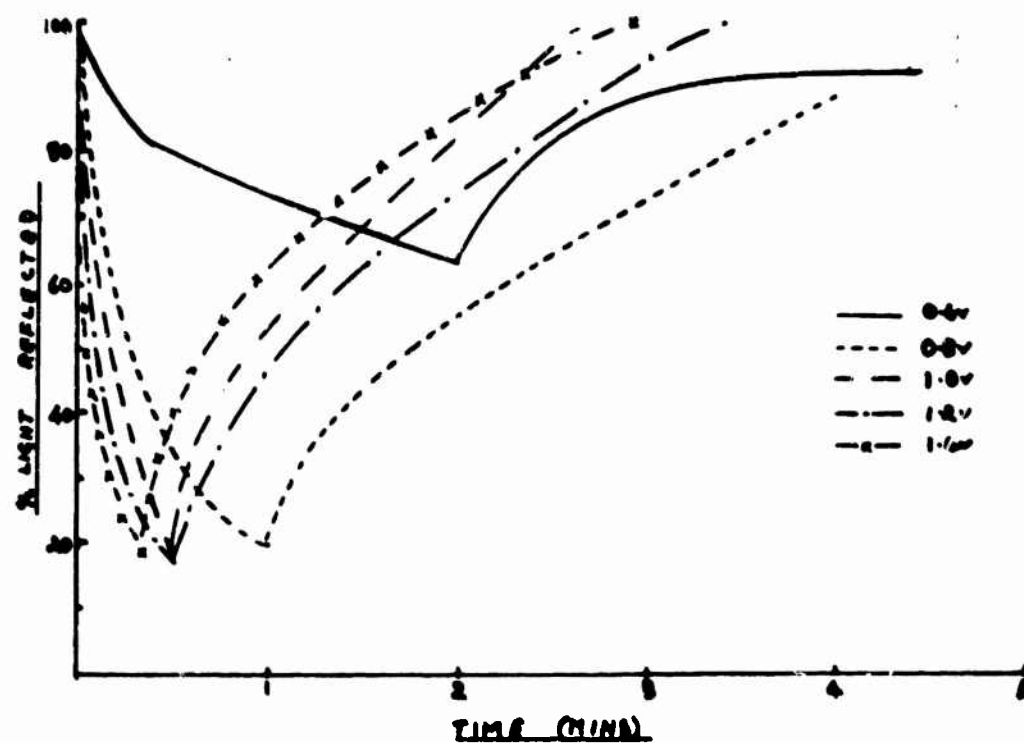


Fig. 108 Light reflected versus time curves for benzyl viologen dichloride with compound (A) and sodium sulphite. A tin oxide transparent cathode and a silver anode.

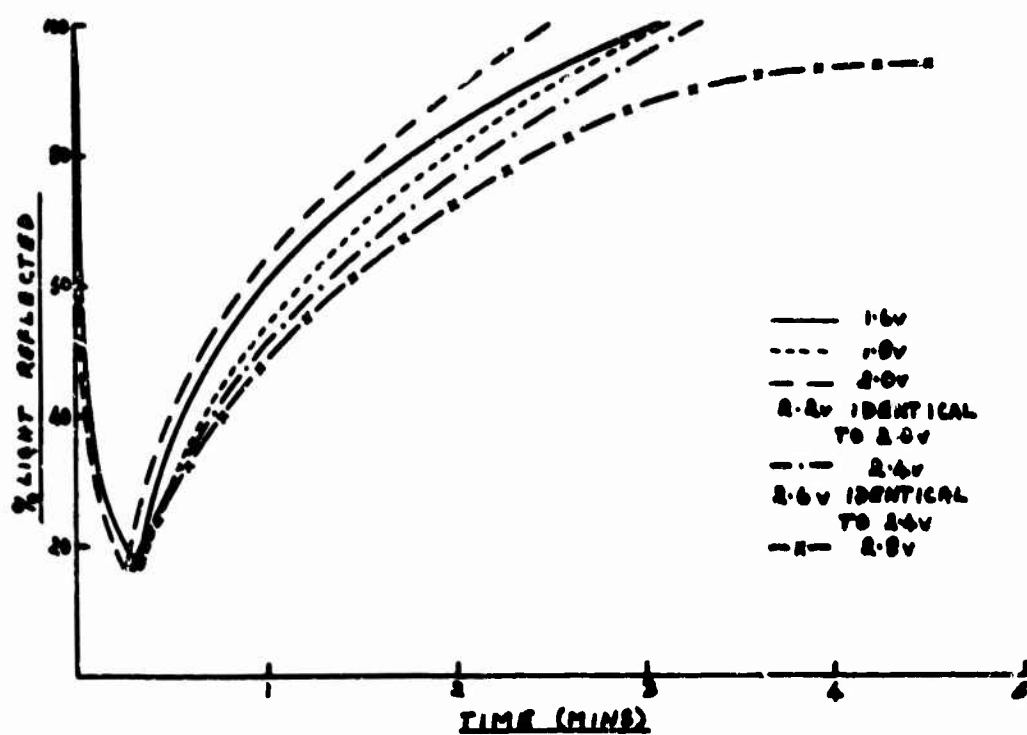


Fig. 109 Light reflected versus time curves for benzyl viologen dichloride with compound (A) and sodium sulphite continued. A tin oxide transparent cathode and a silver anode.

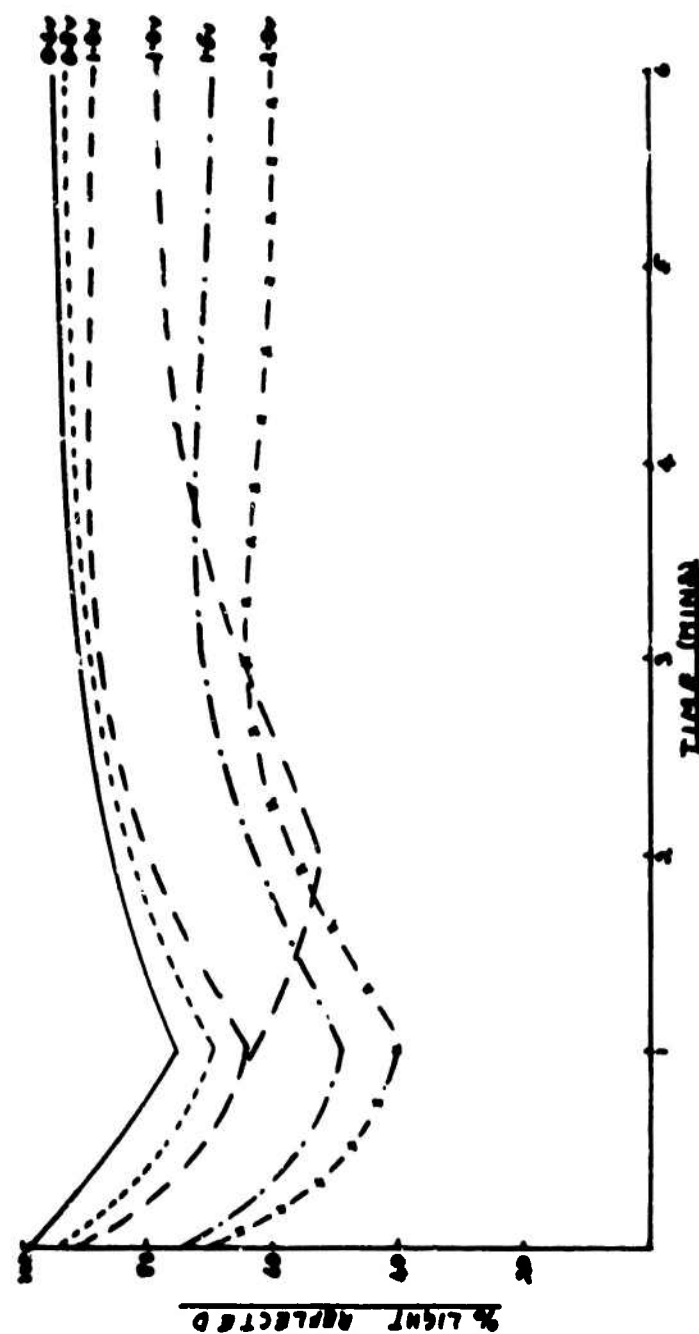


Fig. 110 Light reflected versus time curves for compound (II) with hydroquinone (0.1M). A tin oxide transparent cathode and a silver anode.

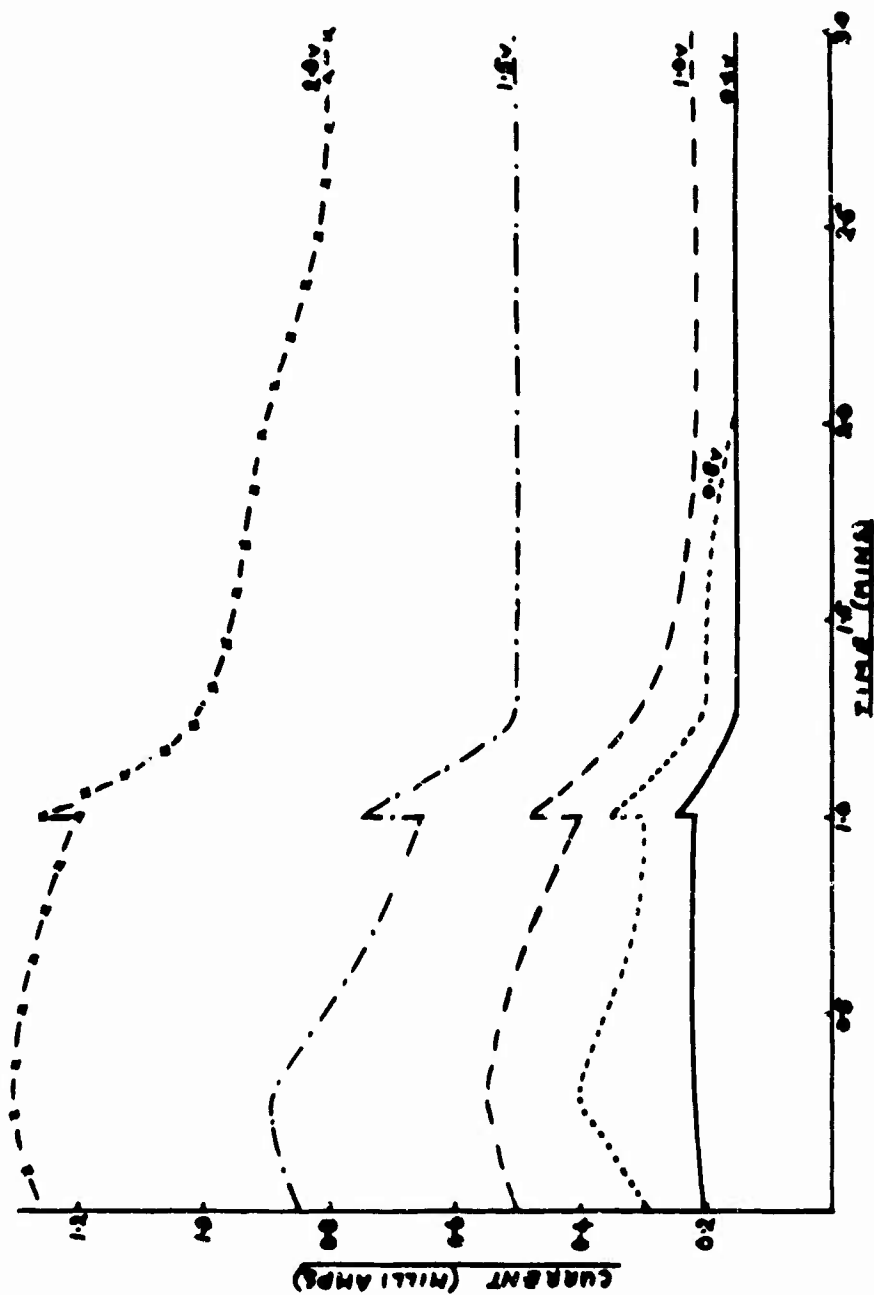


Fig. 111 Current versus time curves for compound (II) with hydroquinone (0.1M). A tin oxide transparent cathode and a silver anode.

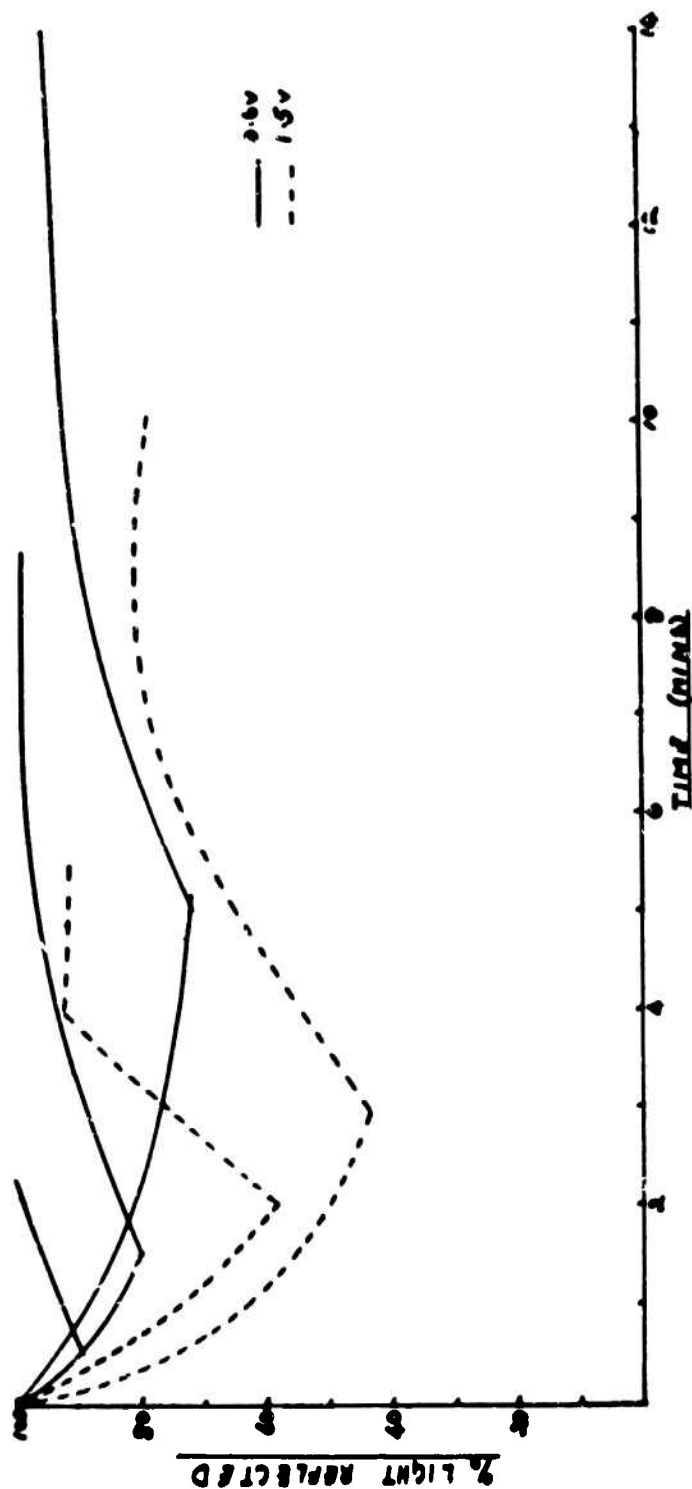


Fig. 112 Light reflected versus time curves for compound (II) with h-droquinone (0.025M). A tin oxide transparent cathode and a silver anode.

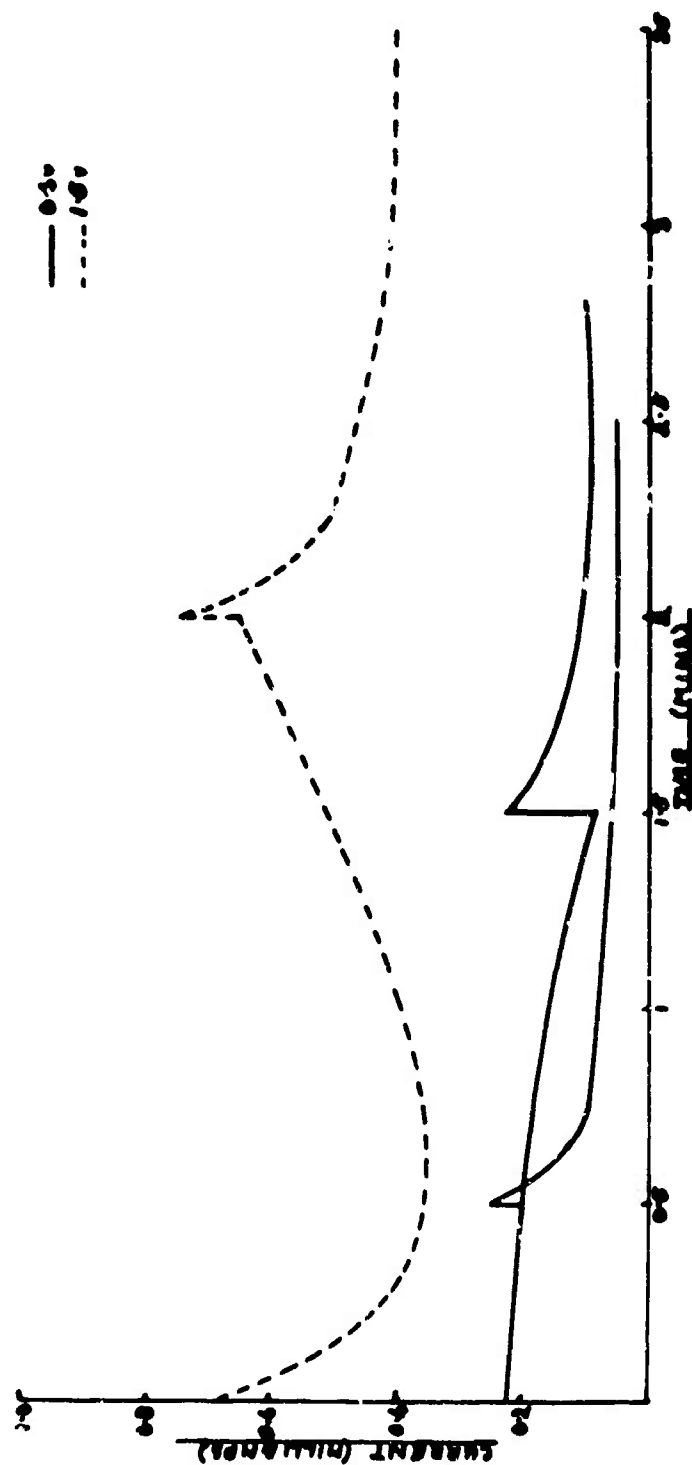
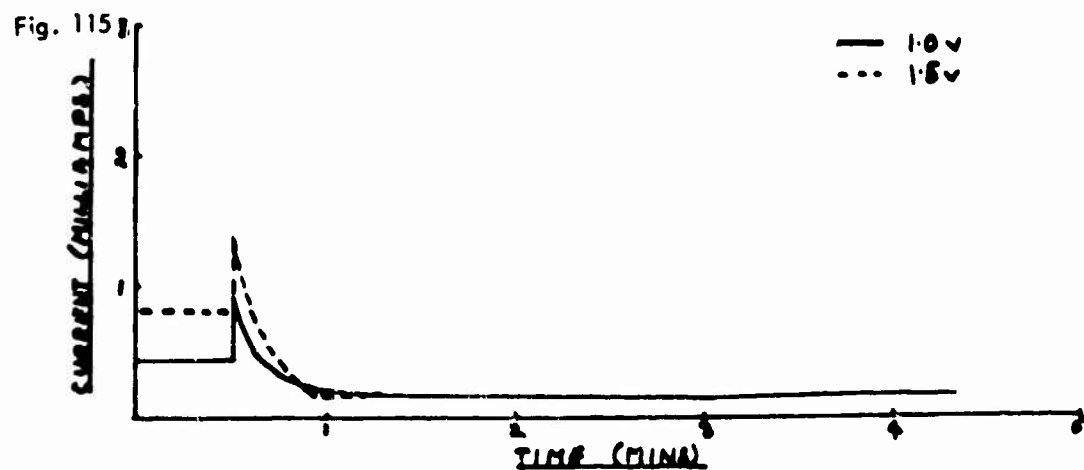
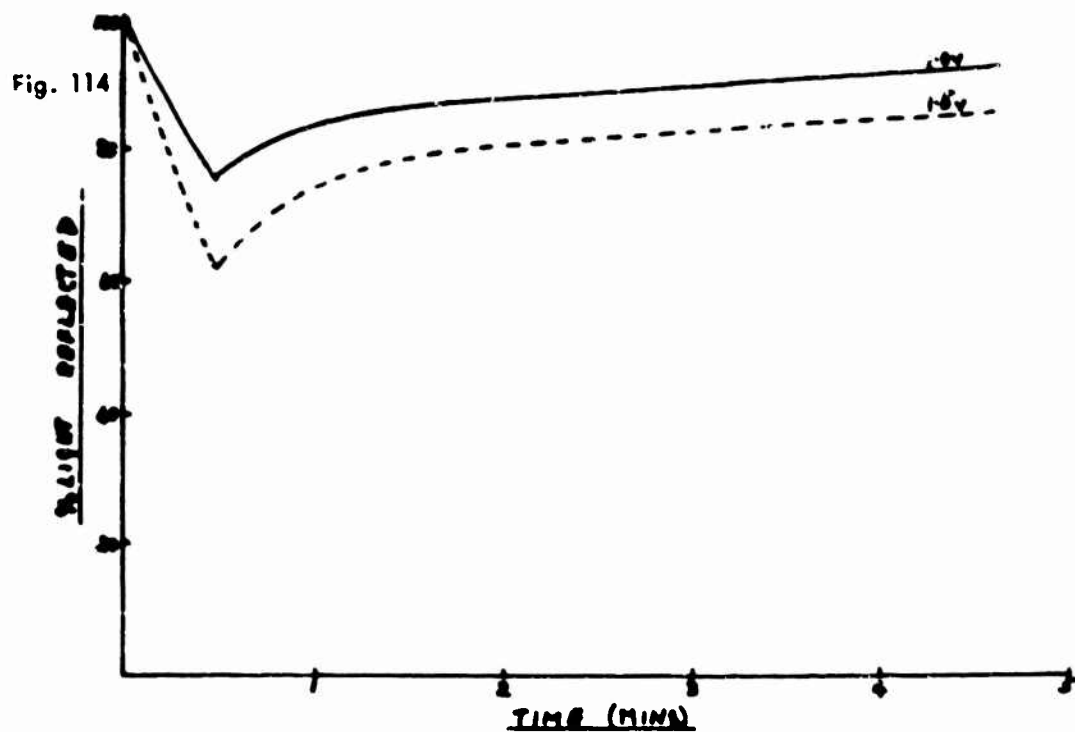
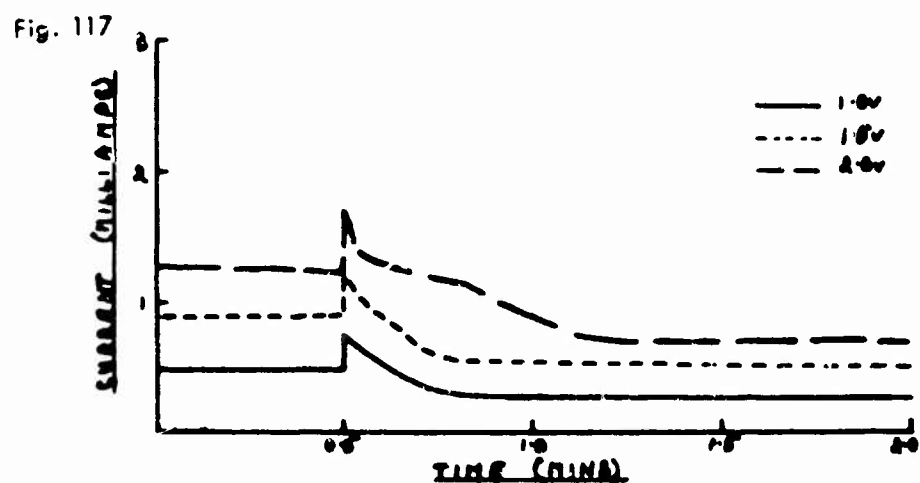
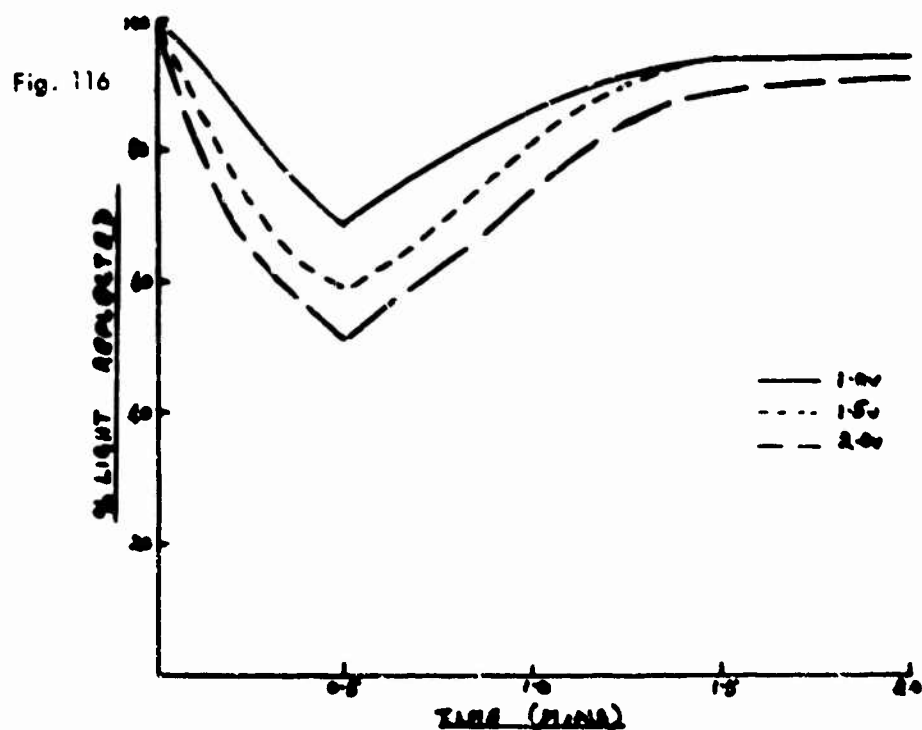


Fig. 113 Current versus time curves for compound (II) with hydroquinone (0.025M). A tin oxide transparent cathode and a silver anode.



Figs. 114 and 115 Light reflected versus time and current versus time curves for compound (IV). A tin oxide transparent cathode and a copper anode.



Figs. 116 and 117 Light reflected versus time and current versus time curves for compound (IV) (0.025M) with potassium ferrocyanide (0.025M). A tin oxide transparent cathode and a copper anode.

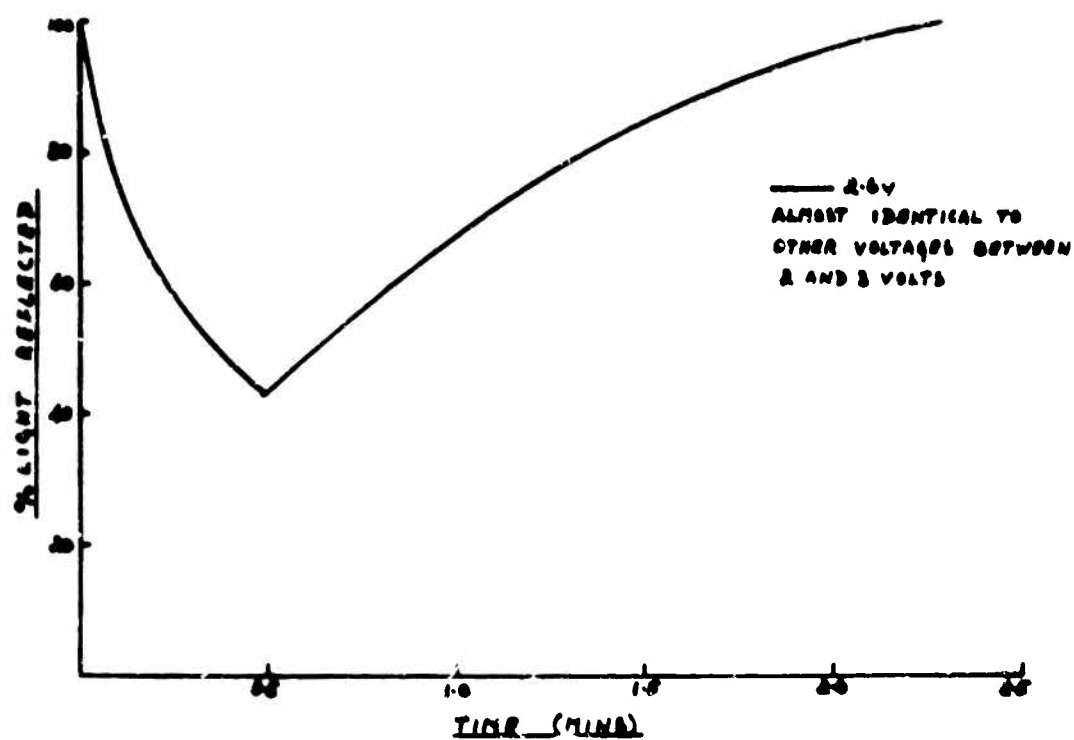


Fig. 118 Light reflected versus time curve for compound (IV). A tin oxide transparent cathode and a silver anode.

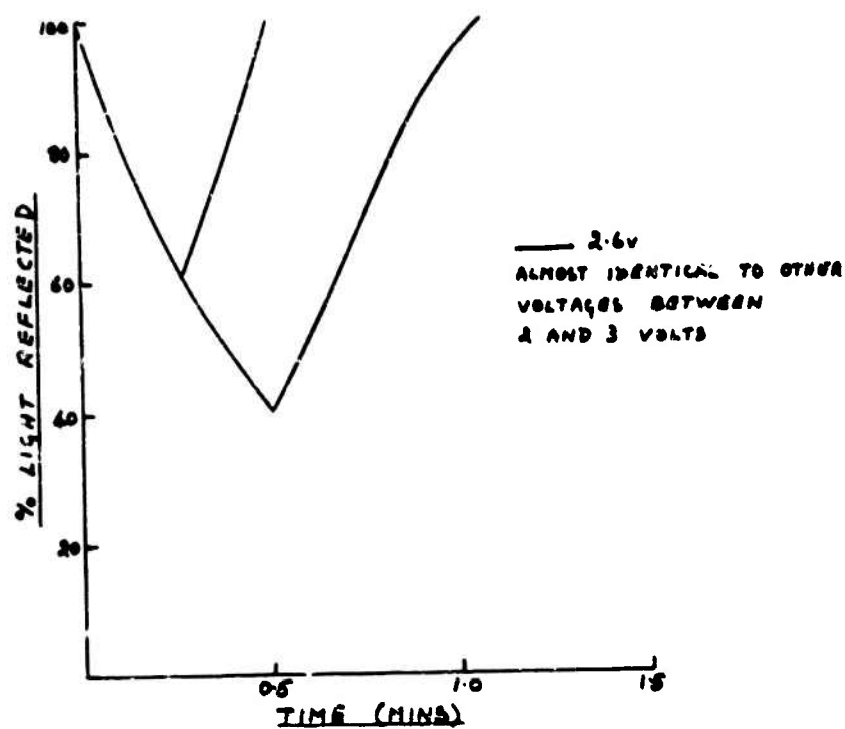


Fig. 119 Light reflected versus time curves for compound (IV) (0.05M) with potassium ferrocyanide (0.025M). A tin oxide transparent cathode and a silver anode.

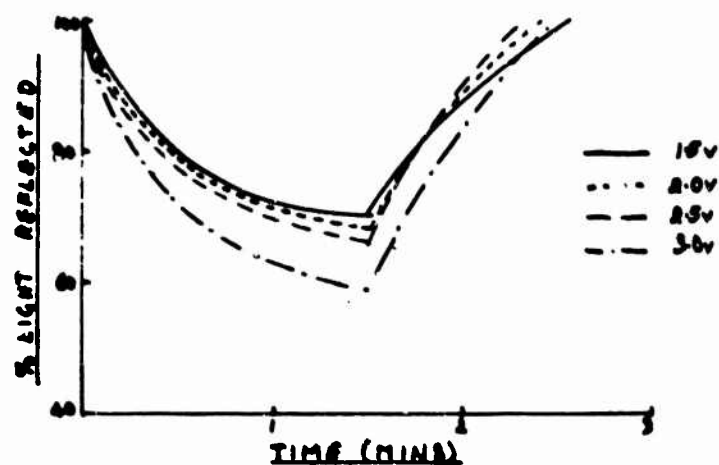


Fig. 120 Light reflected versus time curves for compound (IV) (0.025M) with potassium ferrocyanide (0.025M). A tin oxide transparent cathode and anode.

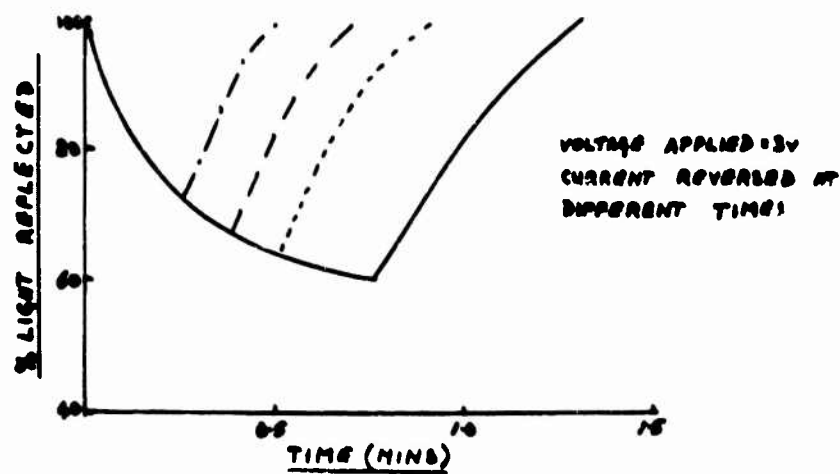


Fig. 121 Light reflected versus time curves for compound (IV) (0.025M) with potassium ferrocyanide (0.025M) at constant voltage. A tin oxide transparent cathode and anode.

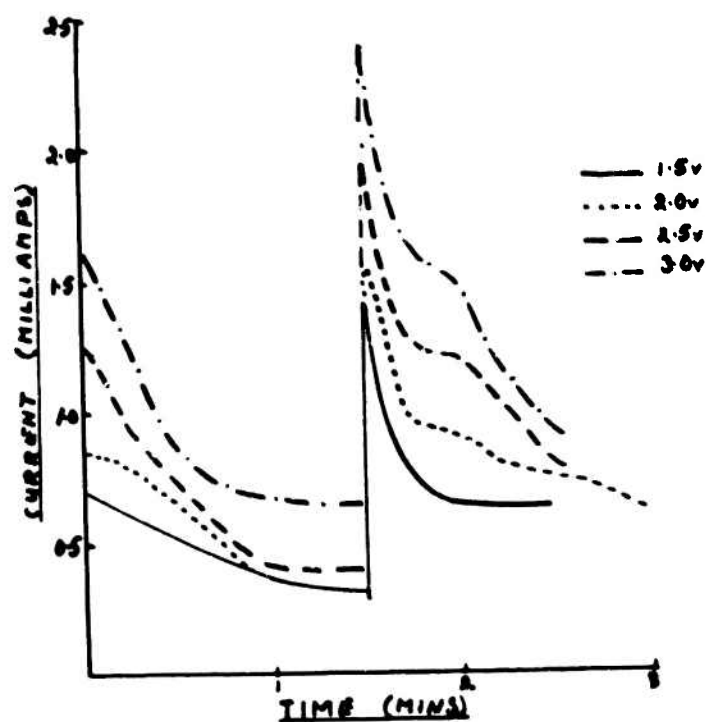


Fig. 122 Current versus time curves for compound (IV) (0.025M) with potassium ferrocyanide (0.025M). A tin oxide transparent cathode and anode.

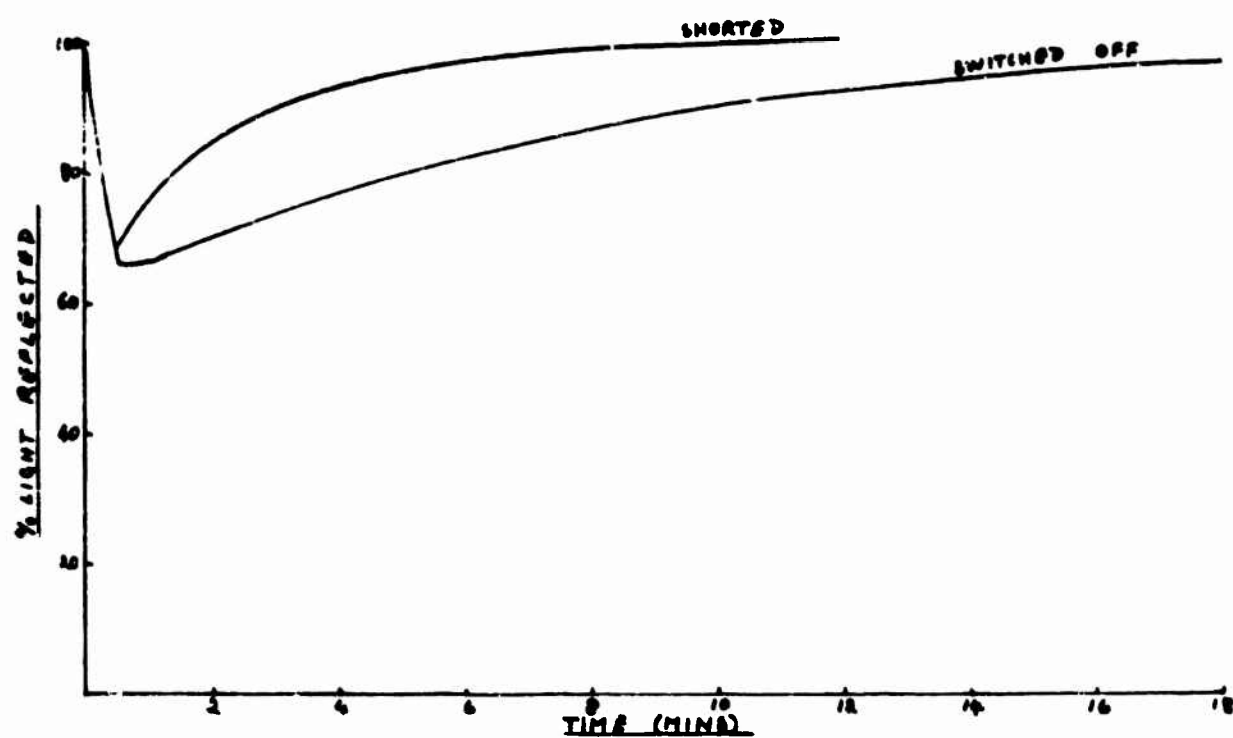


Fig. 123 Light reflected decay curves for compound (IV) (0.025M) with potassium ferrocyanide (0.025M). A tin oxide transparent cathode and anode.